PATENT
CASE 4233C3

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants:	Donald B. Appleby et al	:	Group Art Unit: 1211
Serial No.:	08/360,184	:	Examiner: E. White
Filed:	December 20, 1994	:	
For:	Polyol Polyester Synthesis		

EXHIBITS NUMBERED 1 TO 61

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EXHIBITS

Exhibit No.	Description
1	Continuous Pilot Plant Start-Up Manual, pages Title, ii and 4.1.
2	P90117 Experimental Test Plan.
3	P90117 Control Record, Soap Making and Sucrose Feed Batch.
4	P90117 Control Record, Catalyst Batch.
5	P90117 Process Operating Log Sheets.
6	P90117 Process Log Notebook, January 17-20, 1989.
7	P90117 Data Sheets, Catalyst and Soap.
8	P90117 Data Sheets, Sucrose Esters and I-Bar.
9	P90117 Data Sheets, Unreacted Sucrose.
10	Mattson et al U.S. Patent No. 3,600,186.
11	Rizzi et al U.S. Patent No. 3,963,699.
12	Volpenhein U.S. Patent No. 4,517,360.
13	Revised P90327 Experimental Test Plan.
14	P90327 Run Summary Report.
15	P90424 Experimental Test Plan.
16	Industrial Chemicals Product Development Biweekly Report, Pearson, May 31, 1989.
17	P90605 Experimental Test Plan.
18	Industrial Chemicals Product Development Biweekly Report, Pearson, June 14, 1989.

Exhibit No.	Description
19	Chemicals Product Development Biweekly Report, Pearson, June 28, 1989.
20	P90925 Experimental Test Plan.
21	Chemicals Product Development Division-Food Ingredients Monthly Report, Pearson, October 1, 1989.
22	P00205 Experimental Test Plan.
23	P00326 Experimental Test Plan.
24	DFK Experimental Summary Report, pages 1 and 56-64.
25	Industrial Chemicals Product Development Biweekly Report, Pearson, April 19, 1989.
26	Chemicals Product Development Division-Olestra Process Monthly Report, Pearson, January 1, 1990.
27	Laboratory Notebook SI 6051, pages 6-9.
28	Laboratory Notebook SI 1384, pages 34-39.
29	Laboratory Notebook SI 6044, pages 89-93 and 96.
30	Laboratory Notebook SI 1384, pages 76 and 78-81.
31	Laboratory Notebook SI 6055, pages 24, 25, 28, 32, 33 and 45-47.
32	Laboratory Notebook SI 6055, pages 29, 30, 36-38 and 86-88.
33	Laboratory Notebook SI 6055, pages 55-56.
34	Laboratory Notebook SI 6055, pages 84-85.
35	Laboratory Notebook SI 1373, pages 54 and 57-59.
36	Laboratory Notebook SI 1373, pages 79-81.
37	Laboratory Notebook SI 1373, pages 86-87.
38	Laboratory Notebook, SI 1373, pages 147-154.
39	Industrial Chemicals Product Development Biweekly Report, Corrigan, January 25, 1989.
40	Chemicals Product Development Division Biweekly Report, Corrigan, July 26, 1989.
41	Industrial Chemicals Product Development Biweekly Report, Corrigan, May 17, 1989.

Exhibit No.	Description
42	Chemicals Product Development Division Biweekly Report, Corrigan, August 23, 1989.
43	Chemicals Product Development Division Biweekly Report, Corrigan, September 6, 1989.
44	Chemicals Product Development Division-Olestra Process Monthly Report, Corrigan, March 1, 1990.
45	Development Record No. 7988.
46	Laboratory Notebook SI 1386, pages 40-41 and 44-46.
47	Laboratory Notebook SI 1386, pages 105-107, 111-112 and 114-115.
48	Laboratory Notebook SI 1386, pages 118-139.
49	Industrial Chemicals Product Development Biweekly Report, Kao, February 8, 1989.
50	Laboratory Notebook SI 1367, pages 107, 108 and 111.
51	Laboratory Notebook SI 1367, pages 136-137 and 144-155.
52	Laboratory Notebook SI 1368, page 39.
53	Chemicals Product Development Monthly Report, Kao, November 1, 1989.
54	Industrial Chemicals Product Development Biweekly Report, Schafermeyer, February 22, 1989.
55	Industrial Chemicals Product Development Biweekly Report, Schafermeyer, January 25, 1989.
56	Chemicals Product Development Biweekly Report, Schafermeyer, June 28, 1989.
57	Chemicals Product Development Biweekly Report, Schafermeyer, September 6, 1989.
58	Industrial Chemicals Product Development Division-Food Ingredients Monthly Report, Schafermeyer, October 1, 1989.
59	Interoffice Memorandum, Aylor, July 3, 1990.
60	Interoffice Memorandum, Aylor, July 18, 1990.
61	European Al Publication No. EP 383,404 A1

(1)

Manual # 3

Retention Limit: Until Superseded

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- MUST BE STRICTLY CONTROLLED

CONTINUOUS PILOT PLANT START-UP MANUAL

MWM/elg/4752S

Prepared by

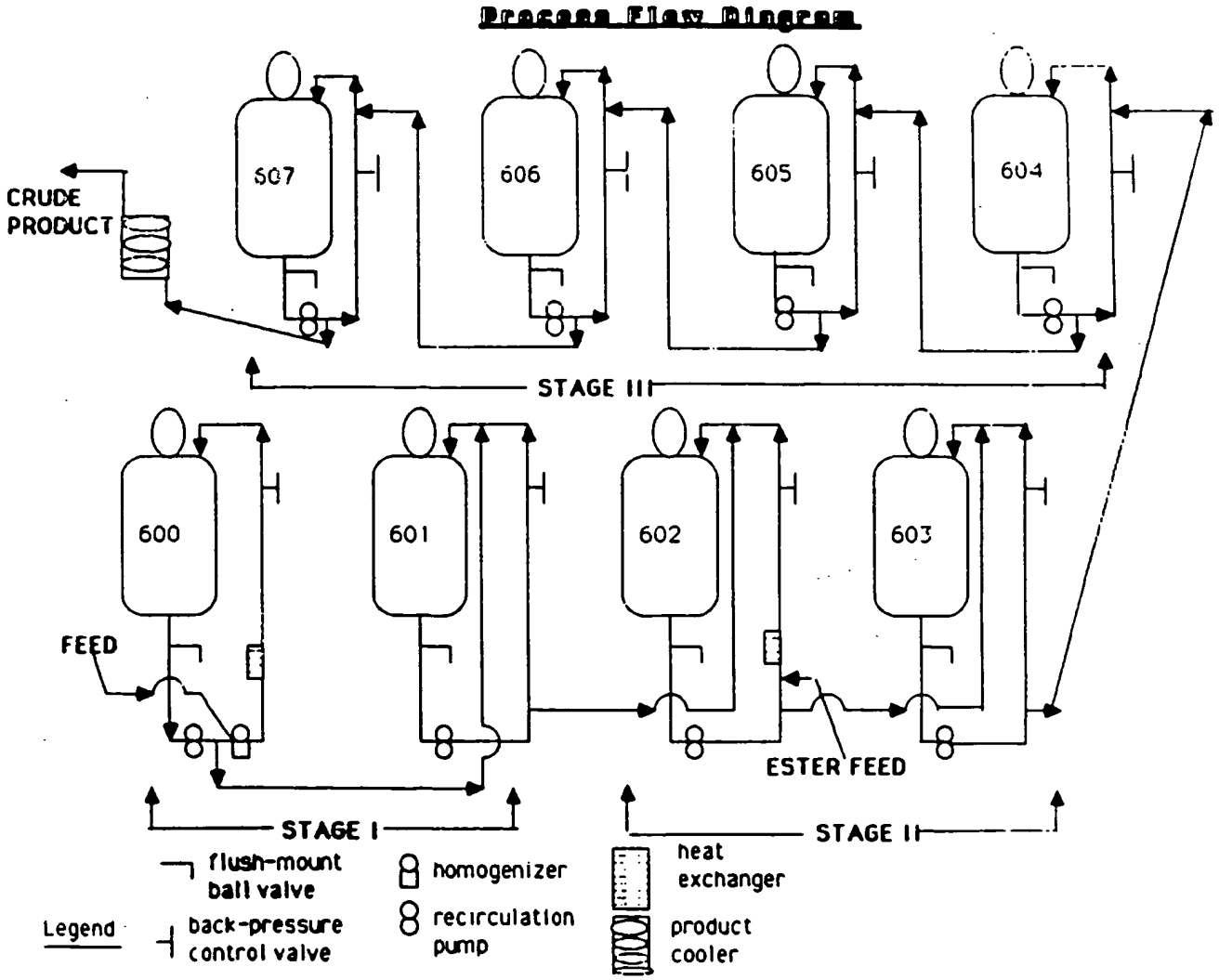
M. W. McIntosh - Manual

G. R. Wyness - Appendices

Industrical Chemicals Division

MWM/elg/4752S

DIAGRAM


Process Flow Diagram
CRUDE PRODUCT
607
606
605
604
STAGE III
600
601
602
603
FEED
ESTER FEED
STAGE I
STAGE II
Legend
flush-mount ball valve
back-pressure control valve
homogenizer
recirculation pump
heat exchanger
product cooler

(2)

INTERDEPARTMENTAL CORRESPONDENCE

From: S. D. Pearson Date: January 12, 1989

To: Distribution Retention Limit: 01/1/90

Subject: **P90117 Experimental Test Plan - Vacuum Requirements Run**

This memo summarizes the run plan for the upcoming 70# run scheduled to start the week of January 17 and run thru the week of January 23.

OBJECTIVE

The specific objectives for this run are:

1) Continue assessment of the 70# process reliability.

2) Evaluate what the vacuum requirements are for stages II & III.

Both of these are key issues to set us up properly for the upcoming Semi-Works run at the end of February. The experiments to accomplish both objectives are straightforward. To assess the reliability we will start-up and run to steady-state twice; once using our standard conditions of 15 mmHg in stage I and full vacuum for the remainder of the reactors, and another time at 1 mmHg in stage II & III. Assuming this is successful,we will have run a total of 3.5 replicate runs with no unexplained aberrations (0.5 from an experiment where only the first three reactors were at steady-state).

The vacuum experiments will be in two parts: in the first, both stage II & III pressure will be maintained at either full vacuum, 1 mmHg, 3 mmHg, or 5 mmHg, while in the second part of the experiment the more normal distinction in pressures between stage II & III will be tried. By allowing the pressure to be constant over stages II & III in the first part we will approach a pseudo-equilibrium point which can be used to infer the correct locations of stages II & III. Recovery from this point and driving the reaction to completion is what we hope to demonstrate from the second part of the vacuum experiments. Please note that some of the run conditions may fulfill more than one part of the objectives.

Completion of the above experiments during the P90117 run will put us in a relatively good position for the Semi-Works run.

EXPERIMENTAL

The run consists of seven experiments; the first and last are start-up and run to steady-state reliability runs, while the other five are aimed at stage II & III vacuum requirements. We will use all the reactors through 607 for all the conditions. As in the past, the catalyst injection system will be used to add all the carbonate and two reactors are planned for stage I (R600 & R601).. The experimental conditions are shown below:

RUN	STAGE I PRESSURE (mm HG)	R600/1/2/3 CATALYST (CYCLE, min)	STAGE I HEIGHT (inches)
ALL	15	11/15/7/7	8

	STAGE II PRESSURE (R602-R603) (mmHg)	STAGE III PRESSURE (R604-R607) (mmHg)
1	FULL VACUUM	FULL VACUUM
2	3	3
3	1	1
4	5	5
5	3	1
6	5	1
7	1	1

A blank will need to be installed in the vacuum header prior to run 5 to allow stage II independence. Run 7 serves as a test for the new mill as well as a replicate, the last sucrose batch will be processed with the new mill. Stage II esters addition will be evenly split between R601 & R602

1. Our efforts for the runs should be focused on the system pressure. **It is critical that the experimental conditions be closely monitored and adhered to.** Please clear all significant deviations from the run plan through me first.

2. Detailed analysis schedules will be posted in the lab. SAMPLES MUST BE TAKEN FROM EVERY ESTER BLEND. WRITE IN LOGBOOK WHENEVER ADDITIONS ARE MADE TO THE CATALYST TANK.

3. Maintain sucrose and catalyst feed under vacuum.

4. The data should be plotted on a control chart. One person on each shift will be responsible for this.

PROPOSED TIMETABLE

Cumulative Time (hr)	Event
0	R600 start-up, use two charges from injector initially, once through foaming turn on injector as reactor is filled
8	R600 through foaming and full, **run 1**, feed to drum
9	feed to R601 and add 1/2 of 2nd stage esters while filling
11	R601 full, feed to drum
12	feed to R602 and start adding remaining 1/2 of 2nd stage esters to 601 while filling
14	R602 full, feed to R603 and continue to fill to R606
22	all reactors full and feeding forward
40	**run 1** complete, start **run 2**
50	start 2nd sucrose feed batch preparation
64	**run 2** complete, start **run 3**
88	**run 3** complete, shut down for Sunday 1/22/89, dump R600
******* SUNDAY **********	
89	start using 2nd sucrose feed batch and proceed with R600 start-up
97	R600 through foaming and full, **run 4**, feed to drum

90	continue to fill to R606, add 2nd stage esters
100	change slurry pump
125	**run 4** complete, install blank in vacuum header, start **run 5**
130	start 2nd catalyst batch preparation
152	**run 5** complete, start **run 6** start 3rd sucrose feed batch preparation, **use new mill** use 2nd catalyst batch
176	**run 6** complete, drain reactors R600-R602
178	R600 start-up, use two charges from injector initially, once through foaming turn on injector as reactor is filled
186	R600 through foaming and full, **run 7**, feed to drum
187	feed to R601 and add 1/2 of 2nd stage esters while filling
189	R601 full, feed to drum
190	feed to R602 and start adding remaining 1/2 of 2nd stage esters to 601 while filling
192	R602 full, feed to R603 and continue to fill to R606
200	all reactors full and feeding forward
218	**run 7** complete

MATERIALS

All feed vessels should be drop tested prior to use. Three sucrose feed batches are necessary, prepared in the following manner:

1. make soap in 001
2. pump 1850# of stage I esters into 001 from 008
3. evaporate methanol
4. pump 1850# of stage I esters into 001 from 008
5. add sucrose
6. pump sucrose slurry from 001 through colloidal mill (@ 1gpm) for first two batches or the new mill for the third batch (@ rate to be determined by S. Pearson) to 026.
7. feed run from 026
8. clean and rinse 001

A tote will be required to feed second stage esters from while making subsequent sucrose batches. For the 2nd and 3rd sucrose batches perform (7) when indicated on the time-line above. Steps 1-7 should be completed in less than 24 hrs. **Vessel 026 should be maintained under vacuum during the run, as well as any sucrose feed batches that are partially complete.** The amount of material, following methanol evaporation, is:

Component	Wt per Batch
Sucrose	800
KOH	115
I-1 (soap)	600
Ester	3700
	5215
Methanol requirements	1200

Two catalyst batches are necessary, prepared in 501, and transferred to the slurry feed tank as required

(times when this transfer is made must be recorded). Pull vacuum on 501 using liquid ring pump. The K2CO3 must be added in 50 # increments, waiting 5 min. between additions with the agitator at 100% and recirculation pump on. **Maintain vacuum and recycle on 501 throughout the course of the run.** Dump and ester rinse 501 prior to making 2nd catalyst batch. The 2nd batch must be made in less than 5hrs to prevent running out of catalyst in the slurry feed tank. The amount of material is:

Component	Wt per Batch
powdered K2CO3	288
Ester	864
	1152

The following is a breakdown of ester requirements for the entire run:

Component	Wt per Batch
Stg I	11,100
Stg II	15,750
Catalyst	1,728

S. D. Pearson

Distribution
R. J. Belanger
D. J. Bruno
D. D. Farris
R. G. Fencl
B. P. Grady
J. K. Howie
Y. Wee
W. J. White
G. R. Wyness
Bldg 96 via C. White

IVORYDALE SOAP PLANT - DEPARTMENT 106
CONTINUOUS PRODUCTION AND CONTROL RECORD

FG-BASE MAKING -------- Page One -------- CRUDE REACTION

Lot Number: P-90117 Mfg. Request Number: _____

SOAP MAKING

Reactor 001

Ingredient	RMC #	Lbs. Req'd	Lbs. Added	Time Added	Date Added	Initials (1 req'd)
I-1	R-81004	600	600	1815	1/17/89	B.G.
Methanol	R-81002	1200	1200#	1800	1/17/89	TA
Potassium Hydroxide	R80505	115	115#	1745	1/17/89	JKP

STAGE ONE FEED

Reactor #001

Ingredient	RMC #	Lbs. Req'd	Lbs. Added	Time Added	Date Added	Initials (1 req'd)
Methyl Ester Blend 1st Pump	R90103	1850	1854	2130	1/17/89	TA
Methyl Ester Blend 2nd Pump	R90103	1850	1853 ~~2~~	2330	1/17/89	[illegible]
Sucrose	R-81005	800	800	2345	1/17/89	KW

Approved by:

T M Wise 2-9-89
Operating Technician Date

Carol L White 2/9/89
Department Manager Date

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IVORYDALE SOAP PLANT - DEPARTMENT 106
CONTINUOUS PRODUCTION AND CONTROL RECORD

FG-BASE MAKING -------- Page Three -------- CRUDE REACTION

Lot Number: P-90117 Mfg. Request Number: _____

in Reactor 501

RECATALYSIS SLURRY

Material	RMC #	Lbs. Req'd	Lbs. Added	Time Added	Date Added	Initials (1 req'd)
for week of 1-17 Ester Blend Y	R90103	750 ~~150~~	750	10:00	1/17/89	LD
Potassium Carbonate	R81006	250 ~~50~~	250	12:30	1/17/89	D.S.
for week of 1-23 Ester Blend Y	R90103	900	900	3:00	1/23/89	MM
Potassium Carbonate	R81006	300	300#	3:30 AM	1-23-89	KMW
Ester Blend						
Potassium Carbonate						
Ester Blend						
Potassium Carbonate						
Ester Blend						
Potassium Carbonate						

Re-catalysis slurry will be made
ester blend. The slurry will cor
methyl ester by weight. The 200
last for 50 to 60 hours at norma
slurry is made weights can be ad
K_2CO_3/75% Methyl Ester ratio.

PROCTER & GAMBLE
ICD-ISP
APPROVED
FOR USE

Raw Material Control No. R81006
Expiration Date: 11/19/89

Approved by:

Not to be used after expiration date:

Signature of person responsible:

Department Manager Date

Operating Technician

IC-005

(5)

FG-Base Pilot Plant
Process Operating Log Sheet

R600
(Take Reading Every Hour)

Date: 1/20/89

Run No. P- 90 117

Date	Time Initial	P.C. 8220 Stage 1 Pressure (mm Hg)	Reactor Temp. (F) TI8600	Vapor Temp. (F) TI8600	Jacket Steam Pressure (psig) PI8600	Recirc. Pressure (psig) PI8640	Heat Exch. Steam Pressure (psig)	Heat Exch. Recirc. Temp. (F) TI8630	Slurry Feed Flowrate (#/hr) FI8650	Feed Pump Speed (Output) FI8650
1/20/89	00[00]	15.2	274.9	174	33.2	46	32	269.9	55.3	43.5
	01[00]	15.2	275.2	173	33.2	45	32	270.1	55.2	43.9
1-20-89	02[00]	15.1	275.1	173	33	43	30	270.1	55.2	44.1
	03[00]	14.9	274.9	173	33.2	46	31	269.9	55.0	44.3
	04[00]	15.3	275.3	173	33	43	31	270.3	54.7	44.8
	05[00]	15.2	275.1	173	33	45	32		54.9	45.4
	06[05]	15.0	275.0	172	33	43	31	269.9	54.9	44.9
	07[00]	14.9	275.1	172	33	42	31	269.9	54.8	45.4
	08[02]	15.2	275.7	171	33	42	31	270.5	54.9	45.3
	0900	15.4	275.1	170	33	41	30	269.9	54	45.2
	10[02]	15.1	275.4	170	33	42	30	270.2	55.3	46.1
	11[00]	15.1	275.1	170	33	43	32		55	46.7
	12	14.5	275.4	170	33	45	31	270.0	55	46.9

FG-Base Pilot Plant
Process Operating Log Sheet

R600
(Take Reading Every Hour)

Date: 1/20/89

Run No. P- 9017

Date	Time Initial	PC8000 Stage 1 Pressure (mm Hg)	Reactor Temp. (F) TI8600	Vapor Temp. (F) TI8600	Jacket Steam Pressure (psig) PI8600	Recirc. Pressure (psig) PI8640	Heat Exch. Steam Pressure (psig)	Heat Exch. Recirc. Temp. (F) TI8630	Slurry Feed Flowrate (#/hr) FI8650	Feed Pump Speed (Output) FI8650
1/20/89	13[00]	14.9	275.3	170	33	46	32	270.2	55.2	46.7
	14[00]	14.7	275.4	170	33	47	32	270.3	550	46.9
	15[00]	14.4	275.2	168	34	44	35	270.0	55.9	46.2
	16[00]	14.7	275.3	168	34	44	32	270.1	54.9	47.6
	17[00]	15.1	275.4	168	34	44	35	270.2	55.3	47.2
	18[00]	15.2	275.3	170	33	45	35	270.2	55.3	47.2
	1900	15.5	275.1	170	33	43	40	269.9	55.1	47.9
	20:00	14.8	275.3	170	33	43	40	270.0	55.8	47.5
	2100	15.9	275.0	168	33	43	40	269.9	55.3	47.5
	2200	15.1	275.3	168	33	43	40	270.1	55.2	47.6
	23:00	15.2	275.4	168	33	43	40	270.1	54.6	48.1
1-20-89	24[00]	15.3	275.3	167	33	43	30	270.1	55.3	47.7

FG-Base Pilot Plant
Process Operating Log Sheet

Catalyst Flowrates
(Take Reading Every Hour)

Date: _____

Run No. P- 90117

		Reactor R600		Reactor R601		Reactor R602		Reactor R603	
Date	Time	Cat. Inj. On ? (Y/N)	Dump Time (min.)	Cat. Inj. On ? (Y/N)	Dump Time (min.)	Cat. Inj. On ? (Y/N)	Dump Time (min.)	Cat. Inj. On ? (Y/N)	Dump Time (min.)
1/19	1500	Y	11	Y	15	Y	7	Y	7
1/19	1600	Y	11	Y	15	Y	7	Y	7
1/19	1700	Y	11	Y	15	Y	7	Y	7
1/19	1800	Y	11	Y	15	Y	7	Y	7
1/19	1900	Y	11	Y	15	Y	7	Y	7
1/19	2300	Y	11	Y	15	Y	7	Y	7
1/20	0000	Y	11	Y	15	Y	7	Y	7
	0100	Y	11	Y	15	Y	7	Y	7
	0200	Y	11	Y	15	Y	7	Y	7
	0300	Y	11	Y	15	Y	7	Y	7
	0400	Y	11	Y	15	Y	7	Y	7

FG-Base Pilot Plant
Process Operating Log Sheet

Catalyst Flowrates
(Take Reading Every Hour)

Date: _____

Run No. P- _____

		Reactor R600		Reactor R601		Reactor R602		Reactor R603	
Date	Time	Cat. Inj. On ? (Y/N)	Dump Time (min.)	Cat. Inj. On ? (Y/N)	Dump Time (min.)	Cat. Inj. On ? (Y/N)	Dump Time (min.)	Cat. Inj. On ? (Y/N)	Dump Time (min.)
12/5/79	1050	Y	11	Y	15	Y	7	Y	7
	0645	Y	11	Y	15	Y	7	Y	7
	1000	Y	11	Y	15	Y	7	Y	7
	2800	Y	11	Y	15	Y	7	Y	7
	0600	Y	11	Y	15	Y	7	Y	7
	1600	Y	11	Y	15	Y	7	Y	7
	1100	Y	11	Y	15	Y	7	Y	7
	1200	Y	11	Y	15	Y	7	Y	7
	1300	Y	11	Y	15	Y	7	Y	7
	1400	Y	11	Y	15	Y	7	Y	7
	1500	Y	11	Y	15	Y	7	Y	7
	1800	Y	11	Y	15	Y	7	Y	7

11-7AM
1-17-89
MON. NIGHT

MADE SOAP IN 001 RX.
ADDED I-1 ESTER TO KOH & MEOH AT 6⁰⁰ AM.
RX 001 REACHED 145° AT 6³⁵ AM
PUMPED ESTER THROUGH RL00, RL01, RL02, RL03, RL04 & RL05.
RL00 & RL01 ARE UNDER VAC. BUT CANNOT GET RX'S TO PULL DOWN PAST 12 MM/HG.
WHEN RL00 WAS FULL OF ESTER IT PULLED DOWN TO 1.7 MLS.
WE SAW A LOT OF BUBBLES LEAKING INTO RX FROM VALVE ON BOTTOM OF RL00.
WE TIGHTEN PACKING & IT HELPED.
I THINK ALL THE PACKING IS TAKEN UP. WE NEED TO REPACK THE VALVE ON THE BOTTOM OF RL00. I THINK.
ESTER CAR IS CIRCULATING ON NORTH 4 SPOT.
RAN A MOISTURE ON I-1 ESTERS BEFORE ADDING TO 001 GOT A .01 MOISTURE

1-17-89
7⁰⁰-15⁰⁰

AT 8⁴⁵ THE KOH LEVEL IN 001 WAS 0.15.
ADDED 2000# OF BLEND Y ESTERS AT 9:15 AND STARTED CIRCULATING THROUGH COMPABLOCK & HEATED UP TO 200°.
TOOK OFF 1030# H_2O. AT 1200 PUT VACUUM ON 001 AND HELD UNDER VACUUM UNTIL 1230. AT 1230 STARTED COOLING 001 SOAP ESTER MIXTURE. OOPS! WHEN WE PUT IN SUCROSE 800 LB WE ALSO PUT IN 32# OF K_2CO_3 BEFORE PUTTING IT THROUGH MILL. PUTTING 001 INTO DRUMS. WILL MAKE A NEW SOAP MAKING WHEN FINISHED. MADE CATALYST SLURRY IN R501 OF 750# BLEND Y ESTER & 250# OF K_2CO_3. PUMPED 5200# OF BLEND Y INTO 008. SAMPLED BLEND Y.

1/17
PS- 23rd
Emptied RX 001 3,191# IN 9 DRUMS
RINSED + DRIED RX 001
SOAP MAKING COMPLETE 21cc - KOH .17
1850# ESTERS added to RX 001 @ 21:30 + STARTED MEOH REMOVAL
FIRST MEOH pump FROM 005 REC 320#
SECOND " " " " " 308#
THIRD " " " " " 473#
TOTAL 1101

1-18-89
11:00-7:00
ADDED 1855# BLEND Y FROM 008 AT 11:30 PM.
ADDED 800# SUCROSE AT 11:45 PM TO 001.
MILL WAS MADE UP, WE TOOK APART + CLEANED + BLEW DRY WITH N_2.
STARTED MILL AT 12:30 AM.
RAN MOISTURE ON 026 + 1½% H_2O
026 IS UNDER FULL VACUUM.
MILL IS STILL GOING INTO 026.
STARTED 026 CIRCULATING OVER TO 70# SYS.
STARTED GOING INTO R600 AT 5:00 AM.
WHAT ARE WE GOING TO DO WITH PRODUCT ~~FROM~~ FROM 001 RX WE PUMPED INTO DRUMS. SCRAP OR SAVE IT.
THERE ARE PLENTY OF SCRAP DRUMS AT CAKE MIX. USE THEM TO SCRAP OUT PRODUCT

11-7 00

STARTED FILLING R600 AT 7:00 AM
1-18-89 LEVEL ON R600 IS SET AT .8".
VACUUM IS SET AT 15 MM/HG.
YOU WILL NEED TO OPEN VALVE GOING TO DRUM WHEN R600 IS FULL.
THERE IS NO STEAM ON JACKET TO R600 YET.

700/1500 Filling up R602 when level is achieved go into a drum for 1 hr then feed forward into R603. Had trouble with R602 discharge pump this morning. Overloads burnt out at MCC. Had to get Sick to change. Everything is running good as of now.

11-7
1-18-89
IT'S RUNNING AS GOOD AS IT GETS.
TAKE SAMPLES EVERY HOUR.
NEXT SET YOU RUN ANALYSIST ON IS 10:00 AM
PRODUCT IS GOING INTO 3605.

1
11/~~10~~/89 3-11
[redacted] TOOK SAMPLE 1600 FOR ME - ALL SIX REACTORS
FOR MEOH
AT 1730 took 24 4oz jar samples R600
R601
to drain temporaries
Control Valve stuck close ~~1650~~ 1730 on R601
Noticed at 1930 => Empty Reactor to correct level
However R601 control valve still messed up stuck open

Finally corrected at 2030 = up to right level
WATCH R602 level!
mclead
Set pressure R602 3 mm Hg = 3.20 on control panel
~~STAGE~~ 2 Transmitter.
At 1100 McLeod = 2.5 Reset transmitter
to 3.35.
Pressure = 3mm Hg McLeod Gauge.

1-20-89
11-7 CLEANED OUT REACTOR COIL AND DRIED
PUT STEAM ON 184 TRAILER

7-3 Any trailer or R.R. car being heated needs to have a thermostatic trap on it, so as to control the temp between 140°-150°.
The coil on trailer # 184 ~~Kellogg~~ Y is broken so thermostatic trap won't work. Steam hose will have to be connected & disconnected as needed to maintain 140°-150° and watched closely so as not to overheat. The side temp indicator on 184 is supposed to be accurate within 5°
The rail cars needs to be disconnected, dome cover removed & buttoned up under N_2 & heat. We will modify dome cover to allow go-devil sampling through the dome cover & gaskets permanently attached.
After blends are pumped we need to shut off recirculation & drain lines. Somehow we are getting O_2 into product, maybe through loose suction fittings.
Please tighten all hose fittings & retape if necessary

Fri
1/20/89

There are vacation request sheets in your mail boxes. Please fill out and return by 2/20/89

Soap making is started in Rx 001 Methanol and K & H has been added. ~~the~~ take first soap sample at 15:00. Need to get esters in from trailer and add to 10000# in 008 for stg I blend. 20#/sp running good.

15:00 23:00 HEATING UP FOR SOAP MAKING
16:00 pumped 3500# ESTER blend FROM TR to 008 REC
18:30 SOAP MAKING COMPLETE) KOH .20%
001 Rx RECYCLE pump FROZE UP (TA Fixed)
MEOH REMOVAL COMPLETE at 20:00
put UNDER FULL VAC FOR 1/2 hr
Added 1850# ESTERS + 800# SUCROSE at 21:30
21:00 STG III PRESSURE SET to 2.3 m.L - CORRESPONDS to 3. mL on McCloud
22:00 - STARTED MILLING FEED FROM Rx 001 to Rx 026
SEWER WOULD NOT TAKE #1 RING pump
1) PULLED VAC ON 001 Rx & CLOSED OFF KEEP POSITIVE PRESSURE ON MILL
PUMPED TOTE BACK to 008 REC - 1157# at 22:00
22:30 STARTED pumping 3000# ESTERS FR TRK to 008 REC - 008 UNDER VAC
WATCH Semiworks Reactor 75-80% Full

BATCH # P90117 DATE STARTED

DATE		1/20/89							1/20/89					
SAMPLE #	Stds	R600	R601	R602	R603	R604	R605	R606	600	601	602	603	604	605	606
SAMPLE TIME	xxxx	820	→	→	→	→	→	→	0600	→	→	→	→	→	→
TECHNICIAN		KMW	KMW	KMW	KMW	KMW	KMW	KMW	KMW	KMW	KMW	KMW	KMW	KMW	KMW
SAMPLE WT. (g)		2.214	2.472	2.540	2.738	2.983	2.441	2.199	2.966	2.848	2.512	2.966	2.776	2.468	2.355
NORMALITY TITRANT															
DATE TITRANT															
BLANK (vol)															
END POINT 1 (vol)		.39	.357	.371	.777	1.083	.437	.47	.283	.488	.741	1.473	1.104	1.015	.822
END POINT 2 (vol)		9.343	7.253	6.872	7.895	8.841	7.137	6.383	12.083	8.369	6.318	8.779	6.124	6.515	5.84
% CARBONATE	xxxx	.24	.20	.48	.49	.50	.36	.29	.13	.24	.41	.29	.55	.57	.48
% SOAP	xxxx	12.41	8.46	6.35	6.94	7.16	7.69	7.92	12.68	8.31	6.16	6.25	4.52	5.83	6.7
% KOH	xxxx														

SOAP MAKING % KOH = $\frac{\text{EP1(vol)}}{\text{SAMPLE WT. (g)}}$ • NORMALITY(HCl) • 5.61

% SOAP = $\frac{\text{EP2(vol)} - \text{EP1(vol)}}{\text{SAMPLE WT. (g)}}$ • NORMALITY(HCl) • 32.0

RXN STAGE II % CARBONATE = $\frac{\text{EP1(vol)}}{\text{SAMPLE WT. (g)}}$ • NORMALITY(HCl) • 13.8

APPROVAL KMW
QUALIFIED TECHNICIAN

(4)

BATCH # P9017 DATE STARTED

DATE		1.20.89													
SAMPLE #	Stds	R600	R601	R602	R603	R604	R605	R606	R600	R601	R602	R603	R604	R605	R606
SAMPLE TIME	xxxx	900							1300						
TECHNICIAN		DRL													
SAMPLE WT. (g)		2.0360	2.0412	2.0373	2.1840	2.0830	2.7100	2.1270	2.2290	2.1882	2.1116	2.1010	2.5086	2.1750	2.1430
NORMALITY TITRANT		.10													
DATE TITRANT		1.11.89													
BLANK (vol)															
END POINT 1 (vol)		.2650	.279	.543	.850	.866	1.012	.810	.299	.145	.371	.436	.694	.588	.589
END POINT 2 (vol)		8.591	6.131	5.024	5.967	5.644	7.654	5.751	9.409	6.673	5.325	5.794	6.903	5.832	5.792
% CARBONATE	xxxx	.18	.19	.37	.54	.57	.52	.53	.19	.09	.24	.29	.38	.37	.38
% SOAP	xxxx	12.69	8.74	6.19	6.25	6.01	6.65	6.21	12.65	9.38	6.95	7.49	7.03	6.85	6.29
% KOH	xxxx														

SOAP MAKING % KOH = $\frac{\text{EP1(vol)}}{\text{SAMPLE WT. (g)}} \cdot \text{NORMALITY(HCl)} \cdot 5.61$

% SOAP = $\frac{\text{EP2(vol)} - \text{EP1(vol)}}{\text{SAMPLE WT. (g)}} \cdot \text{NORMALITY(HCl)} \cdot 32.0$

RXN STAGE II % CARBONATE = $\frac{\text{EP1(vol)}}{\text{SAMPLE WT. (g)}} \cdot \text{NORMALITY(HCl)} \cdot 13.8$

APPROVAL _____
(QUALIFIED TECHNICIAN

BATCH # F70117 DATE STARTED 1/19/89

DATE		1/19/89	1/19/89	1/19/89	1/19/89	1/19/89	1/19/89	1/19/89	1-19-89	1-19-89	1-19-89	1-19-89	1-19-89	1-19-89	
SAMPLE #	Std#	R600	R601	R602	R603	R604	R605	R606	R600	R601	R602	R603	R604	R605	R606
SAMPLE TIME	xxxx	1000	1000	1000	1000	1000	1000	1000	1300	1300	1300	1300	1300	1300	1300
TECHNICIAN		LD	LD	LD	LD	LD	LD	LD	DRL	DRL	DRL	DRL	DRL	DRL	DRL
SAMPLE WT. (g)		2.1671	2.2578	2.0338	2.1693	2.1355	2.0618	2.0335	2.2485	2.1600	2.3033	2.1429	2.5089	2.0742	2.7462
NORMALITY TITRANT		.1	.1	.1	.1	.1	.1	.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
DATE TITRANT		1/11/89	1/11/89	1/11/89	1/11/89	1/11/89	1/11/89	1/11/89	1-11-89	1-11-89	1-11-89	1-11-89	1-11-89	1-11-89	1-11-89
BLANK (vol)															
END POINT 1 (vol)		.507	.421	.806	1.173	.888	1.048	0.904	.427	.410	.762	1.183	1.325	.965	1.329
END POINT 2 (vol)		9.008	6.843	6.232	6.689	4.471	3.085	5.936	9.168	6.574	6.202	6.889	8.050	6.197	8.313
% CARBONATE	xxxx	.32	.26	.55	.77	.57	.70	.61	.26	.26	.46	.76	.73	.64	.67
% SOAP	xxxx	11.80	8.51	7.27	6.45	4.04	1.53	6.50	11.83	8.52	6.50	6.75	6.89	6.58	6.61
% KOH	xxxx														

SOAP MAKING % KOH = $\frac{\text{EP1(vol)}}{\text{SAMPLE WT. (g)}} \cdot \text{NORMALITY(HCl)} \cdot 5.61$

% SOAP = $\frac{\text{EP2(vol)} - \text{EP1(vol)}}{\text{SAMPLE WT. (g)}} \cdot \text{NORMALITY(HCl)} \cdot 32.0$

RXN STAGE II % CARBONATE = $\frac{\text{EP1(vol)}}{\text{SAMPLE WT. (g)}} \cdot \text{NORMALITY(HCl)} \cdot 13.8$

% SOAP = $\frac{\text{EP2(vol)} - 2 \cdot \text{EP1(vol)}}{\text{SAMPLE WT. (g)}} \cdot \text{NORMALITY(HCl)} \cdot 32.0$

APPROVAL D. R. Loggains
(QUALIFIED TECHNICIAN)

(8)

SFC/HPLC RESULTS

DATE 1-20-89
TIME 0400
REACTOR 600
TECHNICIAN P.H.
S.W. 59.0

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
___	10.4	26.3	35.3	22.1	5.9	0	0	0	2.57

HPLC

SE-8

✓

DATE 1-20-89
TIME 0400
REACTOR 601
TECHNICIAN P.H.
S.W. 47.6

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
___	1.5	5.1	15.1	22.9	23.6	20.7	11.3	0	4.27

HPLC

SE-8

✓

DATE 1-20-89
TIME 0400
REACTOR 603
TECHNICIAN P.H.
S.W. ___

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
___	___	___	___	___	___	___	___	___	___

HPLC

SE-8

68.4

DATE 1-20-89
TIME 0700
REACTOR R600
TECHNICIAN dc
S.W. 422

SFC/HPLC RESULTS

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
___	10.4	27.8	36.6	22.1	3.2	0	0	0	2.53

HPLC

SE-8

1.90% Sucrose

B-96
1.47% Sucrose
(Monitor)

___

DATE 1-20-89
TIME 0700
REACTOR R601
TECHNICIAN dc
S.W. 491

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
___	0	6.7	16.3	23.3	20.9	16.8	12.4	3.9	4.37

Sucrose = 0.31%

HPLC

SE-8

B-96
Sucrose = .55%
(monitor)

___

DATE 1-20-89
TIME 0700
REACTOR R605
TECHNICIAN dc
S.W. ___

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
___	___	___	___	___	___	___	___	___	___

HPLC

SE-8

94.08

SFC/HPLC RESULTS

DATE 1-20-89
TIME 1000
REACTOR R600
TECHNICIAN DC
S.W. 45.4

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
___	82	27.5	75.6	27.5	6.2	0	0	0	2.63

HPLC

SE-8

___

DATE 1-20-89
TIME 1000
REACTOR R601
TECHNICIAN DC
S.W. 93.3

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
___	0	3.7	14.8	22.3	21.4	18.6	14.3	4.8	4.59

HPLC

SE-8

___

DATE 1-20-89
TIME 1000
REACTOR R603
TECHNICIAN DC
S.W. ___

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
___	___	___	___	___	___	___	___	___	___

HPLC

SE-8

65.61

DATE 1-20-89
TIME 1300
REACTOR R601
TECHNICIAN AC
S.W. 504

SFC/HPLC RESULTS

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
___	9.9	27.1	36.6	20.9	5.5	0	0	0	2.56

2.09% Sucrose

HPLC

SE-8

___

DATE 1-20-89
TIME 1300
REACTOR R601
TECHNICIAN AC
S.W. 542

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
___	0	6.5	15.0	21.7	21.7	17.7	13.8	14.6	4.44

.19% Sucrose

HPLC

SE-8

___

DATE 1-20-89
TIME 1300
REACTOR R605
TECHNICIAN AC
S.W. ___

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
___	___	___	___	___	___	___	___	___	___

HPLC

SE-8

95.49

SFC/HPLC RESULTS

DATE 1-20-89
TIME 0400
REACTOR 600
TECHNICIAN P.H.
S.W. 59.0

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
___	10.4	26.3	35.3	22.1	5.9	0	0	0	2.57

HPLC

SE-8

✓

DATE 1-20-89
TIME 0400
REACTOR 601
TECHNICIAN P.H.
S.W. 47.6

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
___	1.5	5.1	15.1	22.9	23.6	20.7	11.3	0	4.27

HPLC

SE-8

✓

DATE 1-20-89
TIME 0400
REACTOR 603
TECHNICIAN P.H.
S.W. ___

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
___	___	___	___	___	___	___	___	___	___

HPLC

SE-8

68.4

SFC/HPLC RESULTS

DATE 1-20-89
TIME 0400
REACTOR 603
TECHNICIAN P.H.
S.W. ~

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR

HPLC

SE-8
86.9%

DATE 1-20-89
TIME 0500
REACTOR 602
TECHNICIAN P.H.
S.W. 6.10

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
	0	0	0	3.2	10.8	24.9	38.2	23.0	6.51

HPLC

SE-8
—

DATE 1-20-89
TIME 0500
REACTOR 605
TECHNICIAN P.H.
S.W. —

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR

HPLC

SE-8
92.4%

SFC/HPLC RESULTS

DATE 1-20-89
TIME 0500
REACTOR 606
TECHNICIAN P.H.
S.W. ———

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR

HPLC

SE-8
93.8%

DATE R 1/20/89
TIME 0600
REACTOR 603
TECHNICIAN P.H.
S.W. ———

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR

HPLC

SE-8
64.3

DATE 1-20-89
TIME 0600
REACTOR 604
TECHNICIAN P.H.
S.W. ———

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR

HPLC

SE-8
85.3

SFC/HPLC RESULTS

DATE 1-20-89
TIME 0700
REACTOR R600
TECHNICIAN dc
S.W. 422

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
___	10.4	27.8	36.6	22.1	3.2	0	0	0	2.53

HPLC

SE-8

___

1.90% Sucrose

B-96
1.47% Sucrose
(monitor)

DATE 1-20-89
TIME 0700
REACTOR R601
TECHNICIAN dc
S.W. 491

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
___	0	6.7	16.3	23.3	20.9	16.8	12.4	3.9	4.37

HPLC

SE-8

___

Sucrose = 0.31%

B-96
Sucrose = .55%
(monitor)

DATE 1-20-89
TIME 0700
REACTOR R605
TECHNICIAN dc
S.W. ___

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
___	___	___	___	___	___	___	___	___	___

HPLC

SE-8

94.08

SFC/HPLC RESULTS

DATE 1-20-89
TIME 0700
REACTOR R606
TECHNICIAN [illegible]
S.W. _____

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
___	___	___	___	___	___	___	___	___	___

HPLC

SE-8

93.54 ✓

DATE 1-20-89
TIME 0800
REACTOR R602
TECHNICIAN [illegible]
S.W. 51.2

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
___	0	0	0	2.8	10.7	45.4	38.1	23.0	6.5

HPLC

SE-8

___ ✓

DATE 1-20-89
TIME 0800
REACTOR R603
TECHNICIAN [illegible]
S.W. _____

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
___	___	___	___	___	___	___	___	___	___

HPLC

SE-8

65.90 ✓

SFC/HPLC RESULTS

DATE 1-20-89
TIME 0800
REACTOR RL04
TECHNICIAN JC
S.W. _____

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR

HPLC

SE-8

84.06

DATE 1-20-89
TIME 0900
REACTOR RL05
TECHNICIAN JC
S.W. _____

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR

HPLC

SE-8

93.78

DATE 1-20-89
TIME 0900
REACTOR RL06
TECHNICIAN JC
S.W. _____

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR

HPLC

SE-8

94.21

DATE 1-20-89
TIME 1000
REACTOR R600
TECHNICIAN DC
S.W. 45.4

SFC/HPLC RESULTS

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
___	8.2	27.5	35.6	22.5	6.2	0	0	0	2.63

HPLC

SE-8

___

DATE 1-20-89
TIME 1000
REACTOR R601
TECHNICIAN DC
S.W. 43.3

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
___	0	3.7	14.8	22.3	21.4	18.6	14.3	4.8	4.59

HPLC

SE-8

___

DATE 1-20-89
TIME 1000
REACTOR R603
TECHNICIAN DC
S.W. ___

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
___	___	___	___	___	___	___	___	___	___

HPLC

SE-8

65.61

SFC/HPLC RESULTS

DATE 1-20-89
TIME 1000
REACTOR R604
TECHNICIAN JC
S.W. ———

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
———	———	———	———	———	———	———	———	———	———

HPLC

SE-8

86.46

DATE 1-20-87
TIME 11 AM
REACTOR R602
TECHNICIAN JC
S.W. _____

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
———	0	0	0	3.8	11.7	26.0	37.2	21.2	6.44

HPLC

SE-8

———

DATE 1-20-89
TIME 11 AM
REACTOR R605
TECHNICIAN JC
S.W. _____

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
———	———	———	———	———	———	———	———	———	———

HPLC

SE-8

92.95

SFC/HPLC RESULTS

DATE 1-20-89
TIME 1100
REACTOR R606
TECHNICIAN [illegible]
S.W. _____

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
___	___	___	___	___	___	___	___	___	___

HPLC

SE-8

95.12 ✓

DATE 1-20-89
TIME 1200
REACTOR R603
TECHNICIAN [illegible]
S.W. _____

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
___	___	___	___	___	___	___	___	___	___

HPLC

SE-8

6773

DATE 1-20-89
TIME 1200
REACTOR R604
TECHNICIAN [illegible]
S.W. _____

SFC

%M.E.	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6	SE-7	SE-8	I-BAR
___	___	___	___	___	___	___	___	___	___

HPLC

SE-8

83.60

SUCROSE WORKSHEET

BATCH # P90117

DATE			1/20/89	1/20/89	1.20.89	1.20.89	1.20.89	1.20.89	1.20.89	1.20.89	1.20.89	1.20.89
SAMPLE #	1000 MG/DL STD	2000 MG/DL STD	600	601	R600	R601	R600	R601	R600	R601	R600	R601
SAMPLE TIME	X	X	6:10	6:00	700	700	800	800	900	900	1300	1300
TECHNICIAN			MM	MM	DRL	DRL	DRL	DRL	DRL	DRL	DRL	DRL
STD EXP. DATE												
SAMPLE WT. (G)	X	X	5.1999	5.3270	5.3896	5.4682	5.3540	5.1459	5.3460	5.0832	5.0096	5.2330
SUCR. CONC. (MG/DL)			54	17	79	30	83	24	71	29	70	19
% SUCROSE			1.03	.31	1.47	.55	1.55	.47	1.33	.57	1.39	.36

SIGNED _____
(QUALIFIED TECHNICIAN)

$$\% \text{ FREE SUCROSE} = \frac{\text{SUCROSE (MG/DL)}}{\text{SAMPLE WT. (G)} * 10}$$

(6)

SUCROSE WORKSHEET

BATCH # P90117

DATE			1/19/89	1/19/89	1/19/89	1/19/89	1/19/89	1/19/89	1/19/89	1/20/89	1/20/89	
SAMPLE #	1000 MG/DL STD	2000 MG/DL STD	R600	R601	R600	R601	R600	R601	STD	R600	R601	
SAMPLE TIME	X	X	1300	1300	18^{00}	18^{00}	2300	2300	23^{20}	02^{00}	02^{00}	
TECHNICIAN			LD	LD	CP	CP	JA	TA	CP			
STD EXP. DATE												
SAMPLE WT. (G)	X	X	5.0703	4.9913	4.0091	4.1020	5.4090	6.0621		5.169	4.835	
SUCR. CONC. (MG/DL)			46	15	49	10	60	18		74	18	
% SUCROSE			.907	.30	1.22	.24	~~1.11~~ 1.11	.35	1011	1.4	.37	

STD 995 ck

SIGNED _____
(QUALIFIED TECHNICIAN)

$$\% \text{ FREE SUCROSE} = \frac{\text{SUCROSE (MG/DL)}}{\text{SAMPLE WT. (G)} * 10}$$

United States Patent Office 3,600,186 Patented Aug. 17, 1971

3,600,186

LOW CALORIE FAT-CONTAINING FOOD COMPOSITIONS

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U.S. Cl. 99—1 6 Claims

ABSTRACT OF THE DISCLOSURE

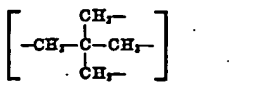
Low calorie food compositions are produced by replacing at least a portion of the fat content of a conventional food with a sugar fatty acid ester or sugar alcohol fatty acid ester having at least 4 fatty acid ester groups with each fatty acid having from 8 to 22 carbon atoms.

BACKGROUND OF THE INVENTION

The field of this invention is food compositions. More specifically, the invention relates to novel fat-containing food compositions where the fat or a portion thereof comprises certain compounds which have the physical properties of ordinary triglyceride fat but which are comparatively less digested or absorbed and thus are relatively low in available calories. One of the most common metabolic problems among people today is obesity. This condition is simply due to a greater intake of calories than are expended. Fat is the most concentrated form of energy in the diet, with each gram of fat supplying approximately 9 calories. Overall, fat constitutes about 40% of the total calories in the diet. If the available calories of a fat could be lowered without decrease in the amount eaten, this would offer a very convenient and practical method by which obesity could be prevented or overcome.

Triglycerides are the main component of edible fat and constitute 90% of the total amount consumed. One method by which the caloric value of edible fat could be lowered would be to decrease the amount of triglyceride that is absorbed in the human system since the usual edible triglyceride fats are almost completely absorbed (see Lipids, 2, H. J. Deuel, Interscience Publishers, Inc., New York 1955, page 215).

The absorbability of triglyceride fat could be decreased by altering either the alcohol or the fatty acid portion of the molecule. There have been some experiments that have demonstrated a decrease in absorbability with certain fatty acids; for example, erucic acid (H. J. Deuel, A.L.S. Cheng, and M. G. Morehouse, Journal Nutrition 35, 295 [1948]) and stearic acid if present as tristearin (F. H. Mattson, Journal of Nutrition 69, 338 [1959]). However, with one exception, no attempt to accomplish this end (decreased absorbability) has been made by altering the alcohol moiety of edible fatty compounds, i.e., fatty acid esters of alcohols. The one exception is U.S. Patent 2,962,419, November 29, 1960, which discloses that fatty acid esters which contain a neopentyl



nucleus are not digested like normal fats and thus can be used as a fat substitute in food compositions.

One of the main problems in attempting to formulate fat compounds that have decreased absorbability and thus low calorie properties is to maintain the desirable

and conventional physical properties of edible fat. Thus, to be a practical low calorie fat, a compound must resemble conventional triglyceride fat, and have the same utility in various fat-containing food compositions such as shortening, margarine, cake mixes, and the like, and be useful in frying or baking.

SUMMARY OF THE INVENTION

In accordance with the present invention, it has been discovered that certain fatty acid ester compounds having at least 4 fatty acid ester groups have the physical properties of ordinary triglyceride fat but are not digested or absorbed to the same extent when eaten. These compounds can therefore be used as a partial or total replacement for ordinary triglyceride fat in fat-containing food compositions to reduce the caloric value thereof. More specifically, the invention provides a low calorie fat-containing food composition wherein from about 10% to about 100% of the total fat comprises a sugar or sugar alcohol fatty acid ester having at least 4 fatty acid ester groups, each fatty acid having from about 8 to about 22 carbon atoms.

The above defined fat-containing food compositions have equivalent physical properties and palatability compared to similar compositions which contain normal triglyceride fat but they have a substantially lower effective caloric value because the specified sugar or sugar alcohol fatty acid esters are less digested or absorbed than normal triglyceride fat in the intestinal tract and hence not all of the ingested calories are available to the body. The sugar or sugar alcohol compounds per se and food compositions containing these compounds which are low in available calories are conveniently referred to herein simply as "low calorie."

DESCRIPTION OF THE PREFERRED EMBODIMENTS.—(LOW CALORIE FAT MATERIALS)

The low calorie fat materials of the present invention are sugar or sugar alcohol fatty acid esters. The term "sugar" is used herein in its conventional sense as generic to mono- and disaccharides. The term "sugar alcohol" is also used in its conventional sense as generic to the reduction product of sugars wherein the aldehyde or ketone group has been reduced to an alcohol. The fatty acid ester compounds are prepared by reacting a monosaccharide, disaccharide or sugar alcohol with fatty acid as discussed below.

Examples of suitable monosaccharides are those containing 4 hydroxyl groups such as xylose, arabinose, and ribose; the sugar alcohol derived from xylose, i.e., xylitol, is also suitable. The monosaccharide erythrose is not suitable for the practice of this invention since it only contains 3 hydroxyl groups; however, the sugar alcohol derived from erythrose, i.e., erythritol, contains 4 hydroxyl groups and is thus suitable. Among 5 hydroxyl-containing monosaccharides that are suitable for use herein are glucose, mannose, gelactose, fructose, and sorbose. A sugar alcohol derived from sucrose, glucose, or sorbose, e.g., sorbitol, contains 6 hydroxyl groups and is also suitable as the alcohol moiety of the fatty acid ester compound. Examples of suitable disaccharides are maltose, lactose, and sucrose, all of which contain 8 hydroxyl groups.

Preferred compounds for use as the alcohol moiety in the low calorie fats of the present invention are selected from the group consisting of erythritol, xylitol, sorbitol, glucose and sucrose.

In preparing the low calorie fats of the present invention at least 4 hydroxyl groups of a sugar or sugar alcohol compound such as those identified above must be esterified with a fatty acid having from about 8 to about 22 carbon

atoms. Examples of such fatty acids are caprylic, capric, lauric, myristic, myristoleic, palmitic, palmitoleic, stearic, oleic, ricinoleic, linoleic, linolenic, eleostearic, arachidic, behenic, and erucic. The fatty acids can be derived from sutiable naturally occurring or synthetic fatty acids and can be saturated or unsaturated, including positional and geometric isomers, depending on the desired physical properties, e.g., liquid or solid, of the fat compound.

Fatty acids per se or naturally occurring fats and oils can serve as the source for the fatty acid component in the sugar or sugar alcohol fatty acid ester. For example, rapeseed oil provides a good source for C_{22} fatty acid. C_{16}–C_{18} fatty acid can be provided by tallow, soybean oil, or cottonseed oil. Shorter chain fatty acids can be provided by coconut, palm kernel, or babassu oils. Corn oil, lard, olive oil, palm oil, peanut oil, safflower seed oil, sesame seed oil, and sunflower seed oil, are examples of other natural oils which can serve as the source of the fatty acid component. Among the fatty acids, those that are preferred have from about 14 to about 18 carbon atoms, and are most preferably selected from the group consisting of myristic, palmitic, stearic, oleic, and linoleic. Thus, natural fats and oils which have a high content of these fatty acids represent preferred sources for the fatty acid components, e.g., soybean oil, olive oil, cottonseed oil, corn oil, tallow and lard.

The sugar or sugar alcohol fatty acid esters suitable for use in this invention can be prepared by a variety of methods well known to those skilled in the art. These methods include: transesterification with another ester such as methyl, ethyl or glycerol, acylation with a fatty acid chloride; acylation with a fatty acid anhydride, and acylation with a fatty acid per se. Further details for making sugar or sugar alcohol fatty acid esters are described in U.S. Patent 2,831,854.

A characterizing feature of the sugar or sugar alcohol fatty acid esters useful in this invention is that they must contain at least 4 fatty acid ester groups. Sugar or sugar alcohol fatty acid ester compounds that contain 3 or less fatty acid ester groups are digested in the intestinal tract much in the manner as ordinary triglyceride fats, but it has been discovered that sugar or sugar alcohol fatty acid ester compounds that contain four or more fatty acid ester groups are digested to a lesser extent and thus have the desired low calories properties for use in this invention. It is not necessary that all of the hydroxyl groups of the sugar or sugar alcohol compound be esterified with fatty acid but it is preferable that the compound contain no more than 2 unesterified hydroxyl groups. Most preferably, all of the hydroxyl groups of the sugar or sugar alcohol are esterified with fatty acid, i.e., the compound is substantially completely esterified. The fatty acid ester groups can be the same or mixed on the same sugar or sugar alcohol molecule.

Thus, to illustrate the above points, sucrose triester of fatty acid would not be suitable for use herein because it does not contain the required 4 fatty acid ester groups. Sucrose tetra fatty acid ester would be suitable but is not preferred because it has more than 2 unesterified hydroxyl groups. Sucrose hexa fatty acid ester would be preferred because it has no more than 2 unesterified hydroxyl groups. An example of a highly preferred compound in which all of the hydroxyl groups are esterified with fatty acid is sucrose octa fatty acid ester. In any given sugar or sugar alcohol fatty acid ester compound the fatty acid ester groups can be selected in view of the desired physical properties of the compound. The sugar or sugar alcohol compounds which contain unsaturated fatty acid ester groups and/or a preponderance of short chain, e.g., $<C_{14}$, fatty acid ester groups are generally liquid at room temperature. The sugar or sugar alcohol compounds which contain long chain fatty acid ester groups, e.g., $>C_{14}$, or are saturated, e.g., stearoyl, are generally solids at room temperatures. Thus, if it is desired to have a liquid low calorie fat, e.g., for use as a salad oil, the sugar or sugar alcohol fatty acid ester can be based on unsaturated fatty acid ester groups such as oleic acid, or can be derived from suitable liquid or partially hydrogenated oils such as soybean oil or olive oil. If it is desired to have a sugar or sugar alcohol fatty acid ester solid at room temperature, the fatty acid ester groups can be saturated, or derived from normally solid fat such as tallow, lard or substantially completely hydrogenated soybean oil.

The following are examples of suitable sugar or sugar alcohol fatty acid esters containing at least 4 fatty acid ester groups suitable for use as low calorie fats in the present invention. Glucose tetraoleate, glucose tetrastearate, glucose tetraester of soybean oil fatty acid, mannose tetraester of tallow fatty acid, galactose tetraester of olive oil fatty acid, aribinose tetraester of cottonseed oil fatty acid, xylose tetralinoleate, galactose pentastearate, sorbitol tetraoleate, sorbitol hexaester of olive oil fatty acid, xylitol pentapalmitate, xylitol tetraester of substantially completely hydrogenated cottonseed oil fatty acid, sucrose tetrastearate, sucrose pentastearate, sucrose hexaoleate, sucrose octaoleate, sucrose octaester of substantially completely hydrogenated soybean oil fatty acid, sucrose octaester of peanut oil fatty acid. As noted before, highly preferred sugar or alcohol fatty acid esters are those wherein the fatty acids contain from about 14 to about 18 carbon atoms and are thus derived from such natural materials as soybean oil and olive oil. Examples of such compounds are erythritol tetraester of olive oil fatty acid, erythritol tetraoleate, xylitol pentaoleate, sorbitol hexaoleate, sucrose octaoleate, and sucrose octaester of soybean oil fatty acid.

The low calorie property of the sugar or sugar alcohol fatty acid ester fats of the present invention is shown below by a fat balance experiment from which a coefficient of absorbability is obtained. This is a conventional experiment in which rats are fed a dietary fat comprising the test material and their feces are collected. The amount of fat eaten and the amount of fat in the feces are determined. The difference between these two values is the amount of fat absorbed. The portion absorbed of the amount fed expressed as a percentage is the coefficient of absorbability and is an indication of the relative available calories of the test materials.

Four low calorie sugar and sugar alcohol fatty acid ester fats of this invention were prepared for this experiment: erythritol tetraoleate; xylitol pentaoleate; sorbitol hexaoleate; and sucrose octaoleate. These compounds were compared with fatty materials containing less than 4 fatty acid ester groups, i.e., with methyl oleate and ethylene glycol dioleate, and with a conventional triglyceride fat, i.e., triolein. The low calorie sugar alcohol fatty acid esters were prepared in the following manner:

Erythritol tetraoleate.—Erythritol and a five-fold excess of ethyl oleate was heated under vacuum during mechanical agitation, in the presence of sodium methoxide catalyst (xylene suspension) over two several hour periods at about 180° C. The reaction product (erythritol tetraoleate) was refined in petroleum ether and crystallized three times from several volumes of acetone at 34° F.

Xylitol pentaoleate.—Xylitol and a five-fold excess of ethyl oleate in dimethyl acid amide (DMAC) solution were heated in the presence of sodium methoxide catalyst (xylene suspension) during mechanical agitation under vacuum over a 5-hour period of about 180° C. During this time the DMCA was distilled off. The product (xylitol pentaoleate) was refined in petroleum ether solution and, after being freed of petroleum ether solution, was separated as a liquid layer four times from acetone at 34° F. and twice from alcohol at 50° F.

Sorbitol hexaoleate was prepared by essentially the same procedure used to prepare xylitol pentaoleate except that sorbitol was substituted for xylitol.

Sucrose octaoleate was also prepared by essentially the same procedure as that used to prepare xylitol pentaoleate except that sucrose was substituted for xylitol.

FAT BALANCE EXPERIMENT

The experimental diet fed to the rats had the composition shown in Table I.

TABLE I (DIET)

Ingredient:	Weight percent
Casein, V.F.	27.0
Sucrose	46.0
Water-soluble vitamins in sucrose No. 18	5.0
Salt mixture USP XIV	4.0
Cellu flour	3.0
Fat	15.0

(Procedure)

Young adult, male, Sprague-Dawley rats were randomly assigned into groups of eight animals each. The animals were housed in individual cages and offered feed and water ad libitum. As noted above, the experimental diet contained 15% fat. 10%, 25%, or 100% of this dietary fat was the test material while the remainder was triolein. The rats were fed the experimental diet during a 5-day orientation period. Throughout the following ten days, food consumption was measured and feces were collected. After collection, the feces were dried to a constant weight, cleaned of hair, weighed and ground. The feces were then submitted for total fatty acid determination by the Saponification Procedure. (See Hoagland, R. and Snider, G. G., U.S.D.A. Technical Bulletin No. 821, March 1942.) Coefficients of absorbability were then calculated. These values were analyzed statistically by an analysis of variance and the Tukey F test.

Because of the large number of dietary fats, it was not possible to feed all fats at the same time. Thus the experiment was carried out in three successive phases. During the first phase, the dietary fat comprising 10% of the test material was fed, in the next phase dietary fat comprising 25% of the test material was fed, and in the final phase, the dietary fat comprised 100% of the test material. Since a group of animals whose dietary fat was solely triolein was used in each phase of the experiment, comparisons among all groups could be made.

(Results)

The coefficients of absorbability of the various dietary fats are given in Table II.

TABLE II

Observed coefficient of absorbability of dietary fats containing triolein plus test materials

Test Material	Level of test material in dietary fat (balance is triolein) 10%	25%	100%
Normal triglyceride fat: Triolein	97	96	96
Comparative fats:			
Methyl oleate	96	96	79
Ethylene glycol dioleate	96	95	87
Low calorie fats:			
Erythritol tetraoleate	(1)	90	68
Xylitol pentaoleate	91	78	53
Sorbitol hexaoleate	86	70	50
Sucrose octaoleate	86	77	61

[1] Not measured.

None of the test materials when they were the sole dietary fat, was as well absorbed as triolein. The addition to triolein of a test material that comprised a sugar or sugar alcohol fatty acid ester having at least 4 fatty acid groups resulted in a decrease in the amount of total fat that was absorbed. This decrease in absorption was related to the level of test material in the total dietary fat. Assuming that the presence of esters of other alcohols, i.e., the test materials, does not alter the absorption of triolein, the absorbability of the test materials per se at each level of total dietary fat was then calculated by the following formula:

$$\frac{\text{Observed coefficient of absorbability} - (\text{percent of triolein in total dietary fat} \times 96\%)}{\text{Percent of test material in total dietary fat}}$$

The results of these calculations are given in Table III.

TABLE III

Calculated coefficients of absorbability of test materials

Test Fat	Level of test material in dietary fat (balance is triolein) 10%	25%	100%
Normal triglyceride fat: Triolein	97	96	96
Comparative fats:			
Methyl oleate	100	96	79
Ethylene glycol dioleate	100	92	87
Low calorie fats:			
Erythritol tetraoleate		72	68
Xylitol pentaoleate	50	24	53
Sorbitol hexaoleate	0	0	50
Sucrose octaoleate	0	20	61

The data in Table III show that as the number of ester groups increase there was a decrease in absorbability. The comparative fats which contained 1 or 2 ester groups were absorbed much like triolein, which contains 3 ester groups. The sugar or sugar alcohol fatty acid esters which contained 4 or more hydroxyl groups were significantly less absorbed. The assumption stated above upon which these calculations were based was confirmed in tests with thoracic, duct cannulated rats using labeled fats. Further, the data of Table III indicate that the xylitol, sorbitol and sucrose esters were better absorbed when they were the sole dietary fat. This observation is consistent with a proposed mechanism which indicates that these compounds compete with the triolein for a single digestive enzyme. The possible mechanism wherein these compounds engage in competition for a common enzyme can be tested by studying hydrolysis of the compounds in vitro. In any event, regardless of the mechanism that is operable, the results obtained in this experiment clearly show that the addition to the diet of a fat comprising a sugar or sugar alcohol fatty acid ester containing at least 4 fatty acid ester groups will result in a decrease in the amount of fat that is absorbed. Thus, these particular fats can be said to be low calorie.

The low calorie sugar or sugar alcohol fatty acid esters of the present invention can be used as a partial or total replacement for normal triglyceride fat in any fat-containing food composition to provide low calorie benefits. In order to obtain a significant low calorie effect, it is necessary that at least about 10% of the fat in the food composition comprises the low calorie sugar or sugar alcohol fatty acid ester. On the other hand, very low calorie and thus highly desirable food compositions of the invention are obtained when the fat comprises up to about 100% of the sugar or sugar alcohol fatty acid ester. Hence, the low calorie fats of the present invention can be used as a partial or complete replacement for normal triglyceride fat in a salad or cooking oil, or a plastic shortening, for use in frying, cake making, bread making, or the like. The low calorie fats can also be used as a partial or complete replacement for normal triglyceride fat in fat-containing food products such as mayonnaise, margarine, and dairy products.

In order to more particularly illustrate the food composition utility of the low calorie fats of the present invention, erythritol tetraester of olive oil fatty acid (ETOFA) was prepared by the following transesterification reaction: Erythritol and distilled and refined ethyl esters of olive oil (100% excess) were mixed with mechanical agitation under vacuum in the presence of sodium methoxide catalyst (xylene suspension) for 14 hours at 100°–180° C. The reaction product was mixed with water and taken up in petroleum ether. After washing to neutrality with aqueous alcohol and water, the petroleum ether was evaporated and the product (ETOFA) was crystallized four times from ten volumes of acetone

at 0° to −10° C. After the last crystallization, the ETOFA was steam deodorized for one hour at about 160° C. to provide a final product having Analytical Data of A.V.—0.1, H.V.—2, TFA—96.6, and TLC—1.0% ethyl ester. The ETOFA was a liquid at room temperature that resembled conventional salad oil in appearance and feel. It was slightly more viscous than conventional salad oil.

ETOFA was shown to function as a typical salad or cooking oil in the following tests, in which it was compared to a conventional commercially available salad oil comprised of refined and lightly hydrogenated soybean oil:

Smoke point.—The smoke point of ETOFA was compared to that of the conventional oil. The ETOFA had a smoke point of about 398° F. as compared to 466° F. for the conventional oil.

Pan frying tests.—Two electric Teflon-coated 10-inch skillets were used for these tests. 200 grams of oil was added to the skillet for the fish and meat test. 30 grams of oil was added for the egg frying test. Temperature for frying was that recommended by the skillet manufacturer for each type of food. ETOFA performed satisfactorily in each of the pan frying tests. Slightly more spattering was observed with the ETOFA than with the conventional oil but it was not deemed excessive.

Eggs—no differences in color or flavor could be detected between the eggs fried in ETOFA and those fried in the conventional oil.

Beefsteaks—ETOFA performed as well as the conventional oil. No differences in color or flavor were detected.

Breaded shrimp—the products fried in ETOFA appeared similar to those fried in conventional oil and were acceptable to a taste panel.

Breaded codfish steaks—ETOFA performed as well as the conventional oil. 66% of a taste panel could not detect any differences. The remaining panelists were split 50/50 among the oil as to preference.

Deep fat frying.—Potato pieces were fried at 375° F. in ETOFA and conventional oil. The ETOFA functioned satisfactorily as a deep frying oil. Panelists judged the products fried in the conventional oil to have a slightly better flavor and color.

Cakes.—High ratio white cakes were prepared using ETOFA, the conventional salad oil, or cottonseed oil as the shortening base. To each base oil was added an emulsification system comprising 14% propylene glycol monostearate and 2.0% stearic acid. (See U.S. Patent 3,145,108.) The cakes had the following formula:

Ingredient:	Weight (grams)
Sugar	133
Flour	107
Shortening	47.5
Double-acting baking powder	6.7
Milk	130
Egg whites	60
Vanilla	2.5

Examination of the cakes indicated that those utilizing ETOFA as a shortening base were substantially equivalent to those based on conventional soybean salad oil or cottonseed oil.

Bread.—ETOFA was substituted for conventional vegetable shortening in normal white bread at an equal weight. Bread prepared with the conventional vegetable shortening was run as a control. The experimental dough containing the ETOFA was very similar to the control in dough handling properties and firming rate of the finished products. The results of a taste panel indicated that there was very little difference in flavor detected with the ETOFA as compared to the vegetable shortening-based bread. The bread formula was as follows:

Ingredient:	Weight (grams)
Flour	808
Wheat starch	146
Water	566
Yeast (dry)	35
Shortening	58
Sucrose	55
Nonfat milk solids	38
Salt	25

Mayonnaise.—ETOFA, conventional soybean salad oil, and cottonseed oil, were compared in a conventional mayonnaise recipe of the following formula:

Ingredient:	Percent by weight
Egg yolk	8.0
Vinegar	11.0
Sugar	2.0
Salt	1.3
Oil	77.7

The ETOFA produced a mayonnaise but it had a slightly more oily taste when compared to that prepared with cottonseed or soybean oil.

Plastic shortening.—100 gram samples of commercially available conventional plastic shortening, ETOFA, and ETOFA+10% hardstock (tristearin) were each melted and plasticized using a laboratory chiller. All samples formed plastic fats.

EXAMPLES

The following examples illustrate low calorie fat-containing food compositions wherein from about 10% to about 100% of the fat comprises a sugar or sugar alcohol fatty acid ester of the present invention.

Example 1.—Salad oils

(A)

Ingredients:	Percent by weight
Refined, bleached, and lightly hydrogenated soybean oil	50
Sucrose octaester of soybean oil fatty acid	50
	100

(B)

Refined cottonseed oil	90.0
Sorbitol pentaoleate	10.0
	100.00

(C)

Sucrose octaoleate	100

(D)

Erythritol tetraester of olive oil fatty acid	100

(E)

50/50 blend of cottonseed oil and soybean oil	50
Olive oil	25
Erythritol tetraester of olive oil fatty acid	25
	100

Example 2.—Plastic shortening

(A)

	Percent by weight
Lightly hydrogenated soybean oil (I.V. 107)	50
Xylitol pentaoleate	40
Tristearin (hardstock, I.V. 8)	10
	100

(B)

50/50 mixture of hardened cottonseed oil and lard	40
Monoglycerides of soybean oil	10
Sucrose octastearate	50
	100

(C)

	Percent by weight
Glucose octaester of tallow fatty acid	100

Example 3.—Prepared cake mix

(a) Specific:	
Cake flour	36
Sugar	44
Shortening (sorbitol hexastearate)	13
Nonfat dried milk solids	4
Leavening	2
Salt	1
	100
(b) General:	
Sugar	35–50
Flour	25–50
Shortening (10%–100% sugar or sugar alcohol fatty acid ester)	5–30
Leavening	1–4
Cocoa	0–7
Egg	0–5
Milk solids	0–5
Flavor	0–5
	100

Example 4.—Prepared icing mix

Shortening (50/50 mixture conventional vegetable shortening and erythritol tetraoleate)	20
Salt	2
Nonfat dry milk solids	5
Sugar	73
	100

Example 5.—Mayonnaise

Fat (75:25 blend of erythritol tetraester of olive oil fatty acid, and refined cottonseed oil)	75
Vinegar	10
Egg yolk	9
Sugar	3
Salt	1
Mustard	1
Flavor	1
	100

Example 6.—Salad dressing

Fat (xylitol pentaoleate)	50
Cornstarch	5
Vinegar	10
Water	35
	100

Example 7.—Margarine

	Percent by weight
Oil (sucrose octaoleate)	80
Milk solids	2
Salt	2
Monoglyceride	15
Water	1
	100

As exemplified above, a wide variety of low calorie fat-containing food compositions can be prepared from the sugar and sugar alcohol esters disclosed herein. Preferred food compositions are those selected from the group consisting of salad oil, plastic shortening, bread, prepared culinary mixes (e.g., for cakes, icings, and the like), mayonnaise, and margarine.

We claim:

1. A low calorie fat-containing food composition comprising non-fat ingredients and fat ingredients wherein from about 10% to about 100% of the total fat consists essentially of a sugar fatty acid ester having at least 4 fatty acid ester groups, each fatty acid having from about 8 to about 22 carbon atoms.

2. The composition of claim 1 wherein the sugar fatty acid ester contains no more than 2 unesterified hydroxyl groups.

3. The composition of claim 2 wherein the sugar fatty acid ester is completely esterified.

4. The composition of claim 3 wherein each fatty acid has from about 14 to about 18 carbon atoms.

5. A low calorie fat-containing food composition comprising non-fat ingredients and fat ingredients wherein from about 10% to about 100% of the total fat comprises a sugar fatty acid ester compound or a sugar alcohol fatty acid ester compound wherein the compound is completely esterified, said compound having at least 4 fatty acid ester groups and each fatty acid having from 8 to 22 carbon atoms.

6. The composition of claim 5 wherein each fatty acid group has from 14 to 18 carbon atoms.

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J. R. HOFFMAN, Assistant Examiner

U.S. Cl. X.R.

99—90, 92, 94, 118, 122, 139, 144

(11)

United States Patent [19]

Rizzi et al.

[11] **3,963,699**

[45] **June 15, 1976**

[54] **SYNTHESIS OF HIGHER POLYOL FATTY ACID POLYESTERS**

[75] Inventors: **George Peter Rizzi; Harry Madison Taylor**, both of Cincinnati, Ohio

[73] Assignee: **The Procter & Gamble Company**, Cincinnati, Ohio

[22] Filed: **Jan. 10, 1974**

[21] Appl. No.: **432,386**

[52] **U.S. Cl.** ..... **260/234 R**; 424/180; 426/611

[51] **Int. Cl.²** **C08B 37/00**

[58] **Field of Search** ..... **260/234 R**

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Primary Examiner—Joseph Paul Brust
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[57] **ABSTRACT**

A solvent-free transesterification comprising the steps of (1) heating a mixture of a polyol, a fatty acid lower alkyl ester, an alkali metal fatty acid soap, and a basic catalyst to form a homogenous melt; and (2) subsequently adding to the reaction product of step (1) excess fatty acid lower alkyl esters yields polyol fatty acid polyesters.

13 Claims, No Drawings

SYNTHESIS OF HIGHER POLYOL FATTY ACID POLYESTERS

BACKGROUND OF THE INVENTION

This invention relates to a high yield synthesis of polyol fatty acid polyesters, sucrose polyesters in particular, via transesterification.

The food industry has recently focused attention on polyol polyesters for use as low calorie fats in food products. As a result of this attention, there is a current need for a high yield synthesis of polyol fatty acid polyesters. Historically, such syntheses have been conducted using a mutual solvent to solubilize a polyol and esters of long-chain fatty acids, thus providing a homogenous reaction medium suitable for catalytic transesterification. One variation of this process, known as the Snell synthesis, has been employed as a means for preparing both poly- and lower esters. However, the solvents heretofore employed in such processes are difficult to separate from the final product and are characteristically toxic, therefore limiting the usefulness of such synthesis in the foods industry. Accordingly, recent efforts have been directed toward the discovery of a high yield synthesis of polyol fatty acid polyesters which does not employ toxic solvents.

Other solvent-free transesterification processes are known in the art.

U.S. Pat. No. 3,521,827 discloses the preparation of sucrose polyesters by means of a solvent-free interesterification using phenyl esters. However, phenol is liberated during the reaction. Phenol is extremely toxic and caustic; contaminates the product; and is difficult to separate. Accordingly, this process does not satisfy current needs for a synthesis of polyol fatty acid polyesters for use in the foods industry.

Feuge, et al., "Preparation of Sucrose Esters by Interesterification", *Journal of the American Oil Chemical Society*, 47[s], 56–60 (1970), disclose a single stage solvent-free transesterification useful in synthesizing fatty acid esters of sucrose. However, this process is limited to the synthesis of lower esters. It has been experimentally determined that if the sucrose/methyl ester ratio of the Feuge, et al., reaction is lowered by use of excess methyl esters in an effort to synthesize polyesters, the reactants will disproportionate and pecipitate sucrose which then caramelizes to form a brittle, charred waste product. Furthermore, the Feuge, et al. article reports low yields using lower alkyl esters. The more successful Feuge, et al. synthesis uses fatty acid methyl carbitol esters as starting materials. Unfortunately, methyl carbitol is, itself, relatively toxic. Thus, the Feuge, et al. process also fails to satisfy current needs for a synthesis of polyol fatty acid polyesters useful in the foods industry.

It is therefore an object of this invention to provide a high yield synthesis of polyol fatty acid polyester.

It is a further object of this invention to provide a synthesis of polyol fatty acid polyesters which does not employ toxic solvent nor generate difficult-to-remove toxic contaminants.

It is a still further object of this invention to provide a synthesis of polyol fatty acid polyesters in which the reactants do not disproportionate thereby reducing caramelization of the polyol.

These and other objects are obtained herein as will be seen from the following disclosure.

SUMMARY OF THE INVENTION

It has now been found that high yields of polyol fatty acid polyesters can be prepared via a transesterification process which can be carried out in the absence of solvents or other contaminants. Thus, the toxicity problems of the prior art are avoided.

The synthesis disclosed herein proceeds in three stages. In the first stage, a heterogenous mixture of a polyol, fatty acid lower alkyl esters, an alkali metal fatty acid soap, and a basic catalyst is reacted to form a homogenous melt consisting of partially esterified polyol and unreacted starting materials. In the second stage, excess fatty acid lower alkyl esters are added to the melt and react with the solubilized partial esters of the polyol and the remaining unesterified polyol to form polyol fatty acid polyester. In the third stage, the polyol fatty acid polyester is separated from the reaction product. The desired polyester product is obtained in high yield. The synthesis can be conveniently carried out at relatively low temperatures and, if desired, at atmospheric pressure.

More specifically, the present invention encompasses a high yield process for synthesizing polyol fatty acid polyesters comprising the steps of:

1. heating a heterogenous mixture comprising: (i) from about 10% to about 50% by weight of a polyol; (ii) from about 40% to about 80% by weight of fatty acid lower alkyl esters; (iii) from about 1% to about 30% by weight of an alkali metal fatty acid soap; and (iv) from about 0.05% to about 5% by weight of a basic catalyst selected from the group consisting of alkali metals, alloys of two or more alkali metals, alkali metal alkoxides and alkali metal hydrides to a temperature of from about 110°C to about 180°C under a pressure of from about 0.1mm Hg to about 760mm Hg for a time sufficient to form a homogenous melt of partially esterified polyol and unreacted starting materials;
2. under the conditions of step 1, adding excess fatty acid lower alkyl esters to the reaction product of step 1 to form the polyol fatty acid polyester; and
3. separating the polyol fatty acid polyester from the reaction mixture.

DETAILED DESCRIPTION OF THE INVENTION

Objects of the present invention are achieved by providing a solvent-free process for synthesizing high yields of polyol fatty acid polyesters. The process is characterized by a unique three step reaction procedure.

Step 1

In the first step of the present process, a heterogenous mixture of (i) a polyol, (ii) fatty acid lower alkyl esters, (iii) an alkali metal fatty acid soap, and (iv) a basic catalyst is reacted to form a homogenous melt comprising partially esterified polyol and unreacted starting materials.

i. As used herein, the term "polyol" is intended to include any aliphatic or aromatic compound containing at least two free hydroxyl groups. In practicing the process disclosed herein, the selection of a suitable polyol is simply a matter of choice. For example, suitable polyols may be selected from the following classes: saturated and unsaturated straight and branched chain linear aliphatics; saturated and unsaturated cyclic aliphatics including heterocyclic aliphatics; or mononu-

clear and polynuclear aromatics including heterocyclic aromatics. Inasmuch as the present invention encompasses a process which does not employ toxic solvents nor generate difficult-to-remove toxic contaminants, preferred polyols are those which have utility in the foods industry. Accordingly, the carbohydrates and non-toxic glycols are preferred polyols. Carbohydrates are polyhydroxy aldehydes or polyhydroxy ketones, or substances that yield such compounds on hydrolysis. They are distributed universally in plants and animals, and make up one of the three important classes of animal foods. Carbohydrates may be subdivided into three important classes; the monosaccharides, oligosaccharides, and the polysaccharides. Monosaccharides include those carbohydrates which do not hydrolyze. Accordingly, monosaccharides suitable for use herein include, for example, glucose, mannose, galactose, arabinose, xylose, ribose, apiose, rhamnose, psicose, fructose, sorbose, tagitose, ribulose, xylulose, and erythrulose. Oligosaccharides are carbohydrates which yield only a few molecules of monosaccharides on hydrolysis. Accordingly, oligosaccharides suitable for use herein include, for example, maltose, kojibiose, nigerose, cellobiose, lactose, melibiose, gentiobiose, turanose, rutinose, trehalose, sucrose, and raffinose. Polysaccharides are those carbohydrates which yield a large number of molecules of monosaccharides on hydrolysis. Accordingly, polysaccharides suitable for use herein include, for example, amylose, glycogen, cellulose, chitin, inulin, agarose, zylans, mannan, and galactans. Another class of polyols preferred herein is the sugar alcohols. Although sugar alcohols are not carbohydrates in a strict sense, the naturally occurring sugar alcohols are so closely related to the carbohydrates that they are also preferred for use herein. The sugar alcohols most widely distributed in nature and suitable for use herein are sorbitol, mannitol, and galactitol. Preferred carbohydrates and sugar alcohols suitable for use herein include, for example, xylitol, sorbitol, and sucrose.

ii. As used herein, the term "fatty acid lower alkyl esters" is intended to include the C_1 and C_2 esters of fatty acids containing about 8 or more carbon atoms, and mixtures of such esters. Suitable esters can be prepared by the reaction of diazoalkanes and fatty acids, or derived by alcoholysis from the fatty acids naturally occurring in fats and oils. If the acids are derived from fats, saturated acids predominate, but if derived from oils, unsaturated acids predominate. Accordingly, suitable fatty acid lower alkyl esters can be derived from either saturated or unsaturated fatty acids. Suitable preferred saturated fatty acids include, for example, capric lauric, palmitic, stearic, behenic, isomyristic, isomargaric, myristic, caprylic, and anteisoarachadic. Suitable preferred unsaturated fatty acids include, for example, maleic, linoleic, licanic, oleic, linolenic, and erythrogenic acids. Mixtures of fatty acids derived from soybean oil, sunflower oil, safflower oil, and corn oil are especially preferred for use herein.

Unusually high yields, i.e., greater than 90%, of polyol fatty acid polyesters have been obtained where methyl esters are used in accordance with the process herein. Accordingly, methyl esters are the preferred fatty acid lower alkyl esters.

iii. As used herein, the term "alkali metal fatty acid soap" is intended to include the alkali metal salts of saturated and unsaturated fatty acids having from about 8 to about 18 carbon atoms. Accordingly, suitable alkai metal fatty acids soaps include, for example, the lithium, sodium, potassium, rubidium, and cesium salts of fatty acids such as capric, lauric, myristic, palmitic, licanic, parinaric, and stearic acids. Mixtures of fatty acids derived from soybean oil, sunflower oil, safflower oil, and corn oil are preferred for use herein. Accordingly, preferred alkali metal fatty acid soaps include, for example, the potassium soap made from soybean oil fatty acids and the sodium soap made from sunflower oil fatty acids.

iv. The basic catalysts suitable for use herein are those selected from the group consisting of alkali metals such as sodium, lithium, and potassium; alloys of two or more alkali metals such as sodium-lithium and sodium-potassium alloys; alkali metal hydrides such as sodium, lithium and potassium hydride; and alkali metal alkoxides such as potassium t-butoxide and sodium methoxide.

In a preferred embodiment of this invention, the catalyst is dispersed in a suitable carrier so as to insure uniform distribution of the catalyst throughout the reaction mass. Suitable carriers or dispersing agents include, for example, mineral oil; hydrocarbon solvents, such as xylene; and polyol octaesters, such as sucrose octaesters. Octaesters derived from the polyol being esterified are preferred carriers since their use avoids contamination or removal problems. Preferred catalysts suitable for use herein include, for example, sodium hydride, potassium hydride, a dispersion of potassium in sucrose octaester, a dispersion of potassium in mineral oil, potassium t-butoxide, and sodium methoxide.

In carrying out step 1, the above-described reactants are combined to form a heterogenous mixture. The precise ratio of reactants can be freely selected from within the guidelines set forth hereinafter. However, routine experimentation may be necessary in order to establish the optimum concentrations for a given set of reactants. In general, the heterogenous mixture comprises from about 10% to about 50%, preferably from about 20% to about 30% by weight of a polyol; from about 40% to about 80%, preferably from about 50% to about 70% by weight of fatty acid lower alkyl esters; from about 1% to about 30%, preferably from about 5% to about 10% by weight of an alkali metal fatty acid soap; and from about 0.05% to about 5%, preferably from about 0.1% to about 0.5% by weight of a basic catalyst selected from the group consisting of alkali metals, alloys of two or more alkali metals, alkai metal alkoxides and alkali metal hydrides. The heterogenous mixture is heated to a temperature within the range of from about 110°C to about 180°C, preferably from about 130°C to about 145°C under a pressure of from about 0.1 mm Hg to about 760 mm Hg. preferably from about 0.5 mm Hg to about 25 mm Hg. Within these temperature and pressure ranges a homogenous melt of partially esterified polyol and unreacted starting materials will form in from about 1 to 4 hours.

It may be desirable to initiate the reaction by initially introducing from about 0.1% to about 1%, by weight, of catalyst and, thereafter, introducing additional catalyst as the reaction proceeds.

Step 2

In the second step of the instant process, excess fatty acid lower alkyl esters are added to the homogenous melt formed in Step 1. As used herein, the term "ex-

cess" is intended to include sufficient lower alkyl esters to raise the overall ester:polyol mole ratio above 10:1, preferably to about 16:1. Although ratios beyond 16:1 can be used, as a general rule, such ratios do not noticeably decrease reaction time or improve the yield and are therefore impractical.

It should be noted that as the transesterification proceeds, a lower alcohol is formed as a by-product. In order to promote the reaction, the alcohol by-product is preferably removed. Many removal techniques are known in the art, any one of which can be used to effectively and efficiently remove the lower alcohol. Vacuum removal both with and without an inert gas sparging has been found to promote the reaction. However, for practical purposes, simple distillation under atmospheric pressure has been found to be sufficient. In any event, the formation of a lower alcohol presents no significant obstacle to the use of the instant process by the foods industry.

Step 3

In the third step of the process, the polyol fatty acid polyesters formed in step 2 are separated from the reaction product containing polyesters, alcohol, and unreacted starting materials. Separation can be accomplished by any of the routinely used separation procedures. Distillation or solvent extraction are preferred due to their simplicity and economy.

The following examples are intended to further clarify the invention and should not be construed as limitations.

EXAMPLE I

Preparation of Sucrose Polyester from Sucrose and Methyl Esters

A 1,000 milliliter resin kettle equipped with a mechanical stirrer, thermometer, dropping funnel, and a distillation head arranged for vacuum take off was charged with finely powdered sucrose (25.5 gram, 0.0745 moles), soy methyl esters (73.5 milliliters, 0.224 moles) and anhydrous potassium-soap made from soy methyl esters (10.0 grams). Heat was supplied via a large magnetically stirred oil bath arranged below the kettle and the mixture was deoxygenated under 15 millimeters vacuum for 1.25 hours at 95°C. On cooling to 55°C sodium hydride, 0.1% (0.178 grams of 56% dispersion in mineral oil) was added and the mixture was reacted at 145°–148°C/15 millimeters for 2 hours during which time the mix changed from a white slurry to a light brown translucent liquid. The mix was cooled to approximately 90°C treated with a second 0.178 gram potion of sodium hydride dispersion and reacted 1.5 hours at 150°C/10 millimeters. The mixture was cooled somewhat, diluted with 297.0 milliliters of methyl esters from soybean oil, reheated to 150°C/10 millimeters for one hour, cooled, treated with a third portion of sodium hydride (0.178 grams), reheated to 150°C/10 millimeters for three hours and finally cooled to room temperature. During 7.5 hours about 25–30 milliliters of liquid distillate collected in vacuum traps at dry iceisopropanol temperature. The crude reaction product was treated with 1 milliliter of acetic acid and washed by stirring and decantation with 5400 milliliters of methanol (9 × 600 milliliters). Ice cooling prior to decantation greatly facilitated the separation of the lower, sucrose polyester phase. The clear brown sucrose polyester phase was freed of last traces of methanol by gentle heat under vacuum prior to bleaching with 10 grams of Filtrol clay at 100°C/2.5 hours/1 atmosphere. The neat mixture of sucrose polyester and clay was cooled, dissolved in hexane and the resulting slurry was vacuum filtered. Evaporation of hexane under vacuum gave 143.2 grams of light yellow oil; having a hydroxyl value of 18.7. The yield based on sugar was 86% sucrose polyesters.

In the above procedure, the sucrose is replaced by an equivalent amount of propylene glycol, glycerol, pentaerythritol, glucose, xylitol and sorbitol, respectively, and the corresponding polyol fatty acid polyesters are obtained.

In the above procedure, the sodium hydride is replaced by an equivalent amount of potassium metal, lithium metal, sodium-potassium alloy, potassium hydride, and lithium hydride, potassium methoxide, and potassium t-butoxide, respectively, and equivalent results are secured.

EXAMPLE II

Preparation of Sucrose Polyester From Sucrose and Soybean Methyl Esters Under Atmospheric Pressure

A mixture containing powdered sucrose (2.52 grams), partially hardened (I.V. 57) soybean methyl esters (6.48 grams) and anhydrous potassium soap made from the same methyl esters (1.0 grams) was homogenized for 10 minutes in a high shear Omnimixer. The slurry was treated with 0.2% by weight of sodium hydride (56% dispersion mineral oil) and reacted 2 hours at 147°C under nitrogen (provision was made for distillation of methanol evolved in the reaction). The one-phase mixture containing lower esters was treated with a second 0.2% of sodium hydride and 31.8 milliliters of additional methyl esters. After reacting another 6 hours at 147°C, the final product was cooled and washed 5 times with 100 milliliters of hot ethanol to remove soap and excess methyl esters. Final removal of ethanol under vacuum gave 15.7 grams of an off-white solid; yield based on sucrose was 90%. Quantitative NMR analysis indicated that the product contained less than 6% methyl ester and TLC showed no free fatty acids present.

As a preferred embodiment of this invention, it has been found that the alkali metal fatty acid soap used herein can be formed in situ by saponifying an alkali metal hydroxide using the fatty acid lower alkyl ester reactant. Accordingly, a preferred embodiment of the process disclosed herein comprises the steps of:

1. Heating a mixture of a fatty acid lower alkyl ester and an alkali metal hydroxide to a temperature of from about 100°C to about 140°C, preferably about 120°C under atmospheric pressure to form an emulsion comprising from about 5% to about 30%, preferably from about 7% to about 15% by weight of the corresponding alkali metal fatty acid soap and lower alkyl ester;

2. Adding to the reaction product of Step (1) from about 10% to about 50%, preferably from about 20% to about 30% by weight of a polyol and from about 0.05% to about 5%, preferably from about 0.1% to about 0.5% by weight of a basic catalyst selected from the group consisting of alkali metals, alloys of two or more alkali metals, alkali metal alkoxides, and alkali metal hydrides to form a heterogenous mixture;

3. Heating the heterogenous mixture formed in Step (2) to a temperature of from about 110°C to about 180°C, preferably from about 130°C to about 145°C

under a pressure of from about 0.1 mm Hg to about 760 mm Hg, preferably from about 0.5 mm Hg to about 25 mm Hg to form a homogenous melt of partially esterified polyol and unreacted starting materials;

4. Under the conditions of Step (3), adding excess fatty acid lower alkyl esters to the reaction product of Step (3) to form the polyol fatty acid polyester; and

5. Separating the polyol fatty acid polyester from the reaction mixture.

The weight percentages of reactants used to form the fatty acid soap emulsion in Step (1) obviously depend upon the molecular weight of the particular alkali metal hydroxide employed. Inasmuch as the alkali metals vary in molecular weight between about 7 (lithium) and about 133 (cesium), the reactant weight preentages vary appreciably. Notwithstanding this variability, calculation of the useful ranges of reactant weight percentages can be determined by routine methods. By way of example, it has been determined that when using potassium hydroxide (molecular weight of about 39), the mixture of Step (1) comprises from about 94% to about 99% by weight fatty acid lower alkyl esters and from about 1% to about 6% by weight potassium hydroxide.

The following example is intended to further clarify the preferred embodiments and should not be construed as a limitation.

EXAMPLE III

Preparation of Sucrose Polyester from Sucrose and Soybean Methyl Esters Using Potassium Dispersion

Soybean methyl esters (2.86 kilograms, I.V. = 132–135) were mixed with potassium hydroxide (63 grams of 85% KOH dissolved in 300 milliliters methanol) at atmospheric pessure and heated to 120°C with agitation. After 2 hours a smooth textured emulsion was formed and powdered sucrose (1.04 kilograms) was added to the mixture. The pressure was reduced to 5 millimeters Hg to remove any moisture and methanol and 30 grams of a potassium dispersion (30% potassium, 70% light mineral oil) was added: This mixture was reacted for 2 hours at 145°C to form a one-phase mixture. Excess soybean methyl esters (12.17 kilograms) were then added and the reaction continued for 4 hours under the above conditions. The system was then allowed to cool overnight and started up the following day by adding more potassium dispersion (30 grams of 30/70 dispersion) and returning to 145°C and 5 millimeters Hg for 4 hours. The reaction mixture was then acidified with glacial acetic acid (250 milliliters). NMR analysis showed the final mixture to contain 49.8% methyl esters. Allowing for the soap formed during the first portion of the reaction and by reaction of the catalyst, this indicates a sucrose polyester yield of 97 to 98% based on sucrose.

In the above procedure, sucrose polyester was prepared without significant caramelization of the sucrose reactant.

In the above procedure, the soybean methyl esters are replaced by an equivalent amount of sunflower oil methyl esters, safflower oil methyl esters, and corn oil methyl esters and the corresponding sucrose fatty acid polyesters are obtained.

Polyol fatty acid polyesters prepared in accordance with the above disclosure are suitable for use as low calorie fats in various food products. For example, U.S. Pat. No. 3,600,186, granted August 17, 1971, teaches the use of polyol fatty acid polyesters as low caloric fats in cooking and salad oils. The following example illustrates low caloric fat-containing food compositions wherein the fat comprises a polyol fatty acid polyester prepared according to the process of the present invention.

EXAMPLE IV

Food Compositions Containing Polyol Fatty Acid Polyesters

Salad oils are prepared as follows:

Ingredients	Percent by Weight
(A)	
Refined, bleached and lightly hydrogenated soybean oil	50
Sucrose octaester of soybean oil fatty acid	50
(B)	
Refined cottonseed oil	90
Sorbitol pentaoleate	10
(C)	
Sucrose octaoleate, 100	
(D)	
Erythritol polyester of olive oil fatty acid	100
(E)	
50/50 Blend of cottonseed oil and soybean oil	50
Olive oil	25
Erythritol polyester of sunflower oil	25

What is claimed is:

1. A solvent-free, low temperature process for synthesizing polyol fatty acid polyesters consisting essentially of:

1. Heating a mixture of a polyol selected from the group consisting of monosaccharides, disaccharides and sugar alcohols, a fatty acid C_{1-2} alkyl ester, an alkali metal fatty acid soap, and a basic catalyst selected from the group consisting of alkali metal, alloys of alkali metals, alkali metal hydrides and alkali metal alkoxides to a temperature of from about 110°C to about 180°C at a pressure of from about 0.1 mm of Hg to about 760 mm of Hg to form a homogenous melt of partially esterified polyol and unreacted starting materials;

2. Under the conditions of Step (1) adding excess fatty acid lower alkyl esters to the reaction product of Step (1) to form the polyol fatty acid polyester; and

3. Separating the polyol fatty acid polyester from the reaction product of Step (2).

2. A process according to claim 1 wherein the polyol is a disaccharide.

3. A process according to claim 1 wherein the polyol is selected from the group consisting of sucrose, xylitol, and sorbitol.

4. A process according to claim 1 wherein the temperature is from about 135°C to about 145°C.

5. A process according to claim 1 wherein the fatty acid C_{1-2} alkyl esters are fatty acid methyl esters.

6. A process according to claim 5 wherein the methyl esters are derived from natural oils selected from the group consisting of soybean oil, sunflower oil, safflower oil and corn oil.

7. A process according to claim 1 wherein the catalyst is selected from the group consisting of potassium hydride, sodium hydride, a dispersion of potassium in sucrose octaester, a dispersion of potassium in mineral oil, potassium t-butoxide and sodium methoxide.

8. A solvent-free, low temperature process for synthesizing polyol fatty acid polyesters consisting essentially of:

1. Heating a mixture comprising (i) from about 10% to about 50% by weight of a polyol selected from the group consisting of monosaccharides, disaccharides and sugar alcohols, (ii) from about 40% to about 80% by weight of fatty acid C_{1-2} alkyl esters, (iii) from about 1% to about 30% by weight of an alkali metal fatty acid soap, and (iv) from about 0.05% to about 5% by weight of a basic catalyst selected from the group consisting of alkali metals, alloy of two or more alkali metals, alkali metal alkoxides, and alkali metal hydrides to a temperature from about 110°C to about 180°C at a pressure of from about 0.1 mm of Hg to about 760 mm of Hg to form a homogenous melt of partially esterified polyol and unreacted starting materials;
2. Under the conditions of Step (1) adding excess fatty acid C_{1-2} alkyl esters to the reaction product of Step (1) to form the polyol fatty acid polyester; and
3. Separating the polyol fatty acid polyester from the reaction product of Step (2.).

9. A process according to claim **8** wherein the polyol is sucrose.

10. A solvent-free, low temperature process for synthesizing poly fatty polyesters consisting essentially of:
1. Heating a mixture of a fatty acid C_{1-2} alkyl ester and an alkali metal hydroxide to a temperature of from about 100°C to about 140°C under atmospheric pressure to form an emulsion comprising from about 5% to about 30%, by weight, of the corresponding alkali metal fatty acid soap and C_{1-2} alkyl ester;
2. Adding to the reaction product of Step (1) from about 10% to about 50% by weight of a polyol and from about 0.05% to about 5% by weight of a basic catalyst selected from the group consisting of alkali metals, alloys of two or more alkali metals, alkali metal alkoxides, and alkali metal hydrides to form a heterogenous mixture;
3. Heating the heterogenous mixture formed in Step (2) to a temperature of from about 110°C to about 180°C under a pressure of from about 0.1 mm Hg to about 760 mm Hg to form a homogeneous melt of partially esterified polyol and unreacted starting materials;
4. Under the conditions of Step (3), adding excess fatty acid C_{1-2} alkyl esters to the reaction product of step (3) to form the polyol fatty acid polyester; and
5. Separating the polyol fatty acid polyester from the reaction mixture.

11. A process according to claim **10** wherein the alkali metal hydroxide is potassium hydroxide.

12. A process according to claim **10** wherein the polyol is sucrose.

13. A process according to claim **10** wherein the fatty acid C_{1-2} alkyl esters are fatty acid methyl esters derived from natural oils selected from the group consisting of soybean oil, sunflower oil, safflower oil, and corn oil.

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(12)

United States Patent [19]

Volpenhein

[11] Patent Number: 4,517,360

[45] Date of Patent: May 14, 1985

[54] SYNTHESIS OF HIGHER POLYOL FATTY ACID POLYESTERS USING CARBONATE CATALYSTS

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[21] Appl. No.: 507,825

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[51] Int. Cl.³ C07H 1/00

[52] U.S. Cl. 536/119; 260/410.6; 536/124

[58] Field of Search 536/119; 260/410.6

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Primary Examiner—Johnnie R. Brown

Attorney, Agent, or Firm—Steven J. Goldstein; Jack D. Schaeffer; Richard C. Witte

[57] ABSTRACT

An improved solvent-free transesterification process for producing polyol fatty acid polyesters is disclosed. In this process, a mixture of a polyol, a fatty acid methyl, 2-methoxy ethyl or benzyl ester, an alkali metal fatty acid soap, and potassium carbonate, sodium carbonate or barium carbonate as a catalyst is heated to form a homogeneous melt. To this melt is subsequently added excess fatty acid methyl, 2-methoxy ethyl or benzyl ester, yielding the desired polyol fatty acid polyesters.

17 Claims, No Drawings

SYNTHESIS OF HIGHER POLYOL FATTY ACID POLYESTERS USING CARBONATE CATALYSTS

TECHNICAL FIELD

This invention relates to an improved, high yield synthesis of higher polyol fatty acid polyesters, sucrose polyesters in particular, via transesterification.

BACKGROUND OF THE INVENTION

The food and pharmaceutical industries have recently focused attention on polyol polyesters for use as low calorie fats in food products and as pharmaceutical agents, e.g., for the lowering of blood cholesterol levels. U.S. Pat. No. 3,600,186, Mattson and Volpenhein, issued Aug. 17, 1971, describes low calorie food compositions formed by replacing at least a portion of the fat content of food products with higher polyol fatty acid polyesters. U.S. Pat. No. 3,954,976, Mattson and Volpenhein, issued May 4, 1976, describes pharmaceutical compositions for inhibiting the absorption of cholesterol comprising effective unit dosage amounts of higher polyol fatty acid polyesters, as well as the method for treating hypercholesterolemia using these polyesters. Additional pharmaceutical uses are described in U.S. Pat. No. 4,241,054, Volpenhein and Jandacek, issued Dec. 23, 1980 (removal of halogenated toxins from the body), and U.S. Pat. No. 4,264,583, Jandacek, Apr. 28, 1981 (treatment of gallstones).

As a result of these many uses for the higher polyol fatty acid polyesters, it would be desirable to have an efficient high yield synthesis for them. Historically, such syntheses have been conducted using a mutual solvent to solubilize a polyol and esters of long chain fatty acids, thus providing a homogeneous reaction medium suitable for catalytic transesterification. One variation of this process, known as the Snell synthesis, has been employed as a means for preparing both poly- and lower esters. However, the solvents employed in such processes are difficult to separate from the final product and are characteristically toxic, therefore limiting the usefulness of such syntheses in the food and pharmaceutical industries. Accordingly, efforts have been directed toward the discovery of high yield syntheses of polyol fatty acid polyesters which do not employ toxic solvents.

BACKGROUND ART

U.S. Pat. No. 3,963,699, Rizzi and Taylor, issued June 15, 1976, describes the basic solvent-free transesterification process for synthesizing higher polyol fatty acid polyesters. In this three-step reaction, a mixture of a polyol (such as sucrose), a fatty acid lower alkyl ester (such as fatty acid methyl ester), an alkali metal fatty acid soap, and a basic catalyst is heated, forming a homogeneous melt, to which is added excess fatty acid lower alkyl ester to form the higher polyol fatty acid polyesters. The polyesters are then separated from the reaction mixture. The catalysts described in this patent as being useful include alkali metals, alloys of two or more alkali metals, alkali metal hydrides, and alkali metal alkoxides. The processes exemplified in this patent utilize sodium hydride, sodium hydroxide or dispersions of potassium as catalysts, and soap:sucrose mole ratios of about 0.3–0.4:1.

Rizzi and Taylor, *Journal of the American Oil Chemists' Society* 55:398 (1978), further describe the reaction set forth in the above-referenced Rizzi and Taylor patent. Advantages are demonstrated for catalyzed reactions versus uncatalyzed reactions; sodium hydride and sodium-potassiun alloy are taught to be effective catalysts. At page 400, the paper teaches that alkali metal carbonates and alkali metal alkoxides are relatively ineffective as catalysts.

U.S. Pat. No. 4,334,061, Brossier, III, issued June 8, 1982, describes a method for separating and purifying the polyesters formed by the Rizzi and Taylor process. The procedure requires, in the separation step, an alkaline pH which is obtained by adding an alkali metal carbonate to the reaction mixture at the conclusion of the transesterification reaction. Thus, the carbonate compounds added do not function as catalysts for the transesterfication reaction.

U.S. Pat. No. 2,893,990, Hass, et al, issued July 7, 1959, describes a process for making carboxylic acid lower esters of sucrose and raffinose; generally, mono- or diesters are formed. In the process, a non-sucrose ester of a fatty acid (e.g., methyl stearate or methyl palmitate) is reacted with sucrose, preferably in a solvent. A wide range of alkaline catalysts, including sodium carbonate and potassium carbonate, are disclosed for use in the reaction.

It has now been found that by modifying the solvent-free transesterfication reaction described in the Rizzi and Taylor patent, discussed above, using potassium carbonate, sodium carbonate or barium carbonate as the catalyst and/or using significantly higher soap:sucrose mole ratios than those originally envisioned, shorter reaction times, more complete utilization of the polyol component, and improved yields of the higher polyol polyesters can be obtained.

It is, therefore, an object of this invention to provide an improved solvent-free high yield synthesis of polyol fatty acid polyesters.

SUMMARY OF THE INVENTION

The present invention encompasses an improved solvent-free transesterification process for synthesizing higher polyol fatty acid polyesters comprising the steps

(1) heating a mixture of (a) a polyol selected from the group consisting of monosaccharides, disaccharides and sugar alcohols, (b) a fatty acid ester selected from the group consisting of methyl esters, 2-methoxy ethyl esters, benzyl esters and mixtures thereof, (c) an alkali metal fatty acid soap, and (d) a basic catalyst, to a temperature of from about 110° C. to about 180° C. at a pressure of from about 0.1 mm to about 760 mm of mercury to form a homogenous melt; and

(2) subsequently adding to the reaction product of step (1) excess fatty acid ester selected from the group consisting of methyl esters, 2-methoxy ethyl esters, benzyl esters and mixtures thereof;

the improvement being obtained by utilizing a basic catalyst component selected from the group consisting of potassium carbonate, sodium carbonate, barium carbonate and mixtures thereof. The preferred catalyst is potassium carbonate.

In a particularly preferred embodiment, the present invention further encompasses an improved solvent-free transesterification process for synthesizing higher polyol fatty acid polyesters comprising the steps of:

(1) heating a mixture of (a) a polyol selected from the group consisting of monosaccharides, disaccharides and sugar alcohols, (b) a fatty acid ester selected from the group consisting of methyl esters, 2-methoxy

ethyl esters, benzyl esters and mixtures thereof, (c) an alkali metal fatty acid soap, and (d) a basic catalyst, to a temperature of from about 110° C. to about 180° C. at a pressure of from about 0.1 mm to about 760 mm of mercury to form a homogeneous melt; and

(2) subsequently adding to the reaction product of step (1) excess fatty acid ester selected from the group consisting of methyl esters, 2-methoxy ethyl esters, benzyl esters and mixtures thereof;

the improvement being obtained by using molar ratios of soap:polyol in step (1) of from about 0.6:1 to about 1:1, preferably from about 0.75:1 to about 1:1, more preferably from about 0.75:1 to about 0.85:1, most preferably about 0.75:1.

DETAILED DESCRIPTION OF THE INVENTION

The present invention encompasses improvements in the solvent-free transesterification reaction for forming higher polyol fatty acid polyesters described and claimed in U.S. Pat. No. 3,963,699, Rizzi and Taylor, issued June 15, 1976, incorporated herein by reference. This process is characterized by a three-step reaction procedure, summarized below. By utilizing the improvements taught herein, the reaction described in the Rizzi and Taylor patent can be improved by reducing excessive foaming, shortening reaction times, increasing the yields of the higher polyol fatty acid polyesters, and yielding products having better (lighter) color characteristics. In fact, the improvements herein permit the reaction to be formulated as a single step solvent-free reaction for the production of higher polyol fatty acid polyesters.

STEP 1

In the first step of the present process, a heterogeneous mixture of a polyol, fatty acid methyl, 2-methoxy ethyl or benzyl esters, an alkali metal fatty acid soap, and a basic catalyst is reacted to form a homogeneous melt comprising partially esterified polyol and unreacted starting materials.

As used herein, the term "polyol" is intended to include any aliphatic or aromatic compound containing at least two free hydroxyl groups. In practicing the process disclosed herein, the selection of a suitable polyol is simply a matter of choice. For example, suitable polyols may be selected from the following classes: saturated and unsaturated straight and branched chain linear aliphatics; saturated and unsaturated cyclic aliphatics, including heterocyclic aliphatics; or mononuclear or polynuclear aromatics, including heterocyclic aromatics. Carbohydrates and non-toxic glycols are preferred polyols. Monosaccharides suitable for use herein include, for example, mannose, galactose, arabinose, xylose, ribose, apiose, rhamnose, psicose, fructose, sorbose, tagitose, ribulose, xylulose, and erythrulose. Oligosaccharides suitable for use herein include, for example, maltose, kojibiose, nigerose, cellobiose, lactose, melibiose, gentiobiose, turanose, rutinose, trehalose, sucrose and raffinose. Polysaccharides suitable for use herein include, for example, amylose, glycogen, cellulose, chitin, inulin, agarose, zylans, mannan and galactans. Although sugar alcohols are not carbohydrates in a strict sense, the naturally occurring sugar alcohols are so closely related to the carbohydrates that they are also preferred for use herein. The sugar alcohols most widely distributed in nature and suitable for use herein are sorbitol, mannitol and galactitol.

Particularly preferred classes of materials suitable for use herein include the monosaccharides, the dissacharides and sugar alcohols. Preferred carbohydrates and sugar alcohols include xylitol, sorbitol and sucrose.

As used herein, the term "fatty acid esters" is intended to include the methyl, 2-methoxy ethyl and benzyl esters of fatty acids containing about eight or more carbon atoms, and mixtures of such esters. Suitable esters can be prepared by the reaction of diazoalkanes and fatty acids, or derived by alcoholysis from the fatty acids naturally occurring in fats and oils. Suitable fatty acid esters can be derived from either saturated or unsaturated fatty acids. Suitable preferred saturated fatty acids include, for example, capric, lauric, palmitic, stearic, behenic, isomyristic, isomargaric, myristic, caprylic, and anteisoarachadic. Suitable preferred unsaturated fatty acids include, for example, maleic, linoleic, licanic, oleic, linolenic, and erythrogenic acids. Mixtures of fatty acids derived from soybean oil, palm oil, sunflower oil, safflower oil, and corn oil are especially preferred for use herein. Methyl esters are the preferred fatty acid esters for use herein, since their use in the process herein tends to result in unusually high yields of polyol fatty acid polyesters.

As used herein, the term "alkali metal fatty acid soap" is intended to include the alkali metal salts of saturated and unsaturated fatty acids having from about eight to about eighteen carbon atoms. Accordingly, suitable alkali metal fatty acid soaps include, for example, the lithium, sodium, potassium, rubidium, and cesium salts of fatty acids such as capric, lauric, myristic, palmitic, licanic, parinaric, and stearic acids, as well as mixtures thereof. Mixtures of fatty acids derived from soybean oil, sunflower oil, safflower oil, and corn oil are preferred for use herein. Accordingly, preferred alkali metal fatty acid soaps include, for example, the potassium soap made from soybean oil fatty acids and the sodium soap made from sunflower oil fatty acids.

The basic catalysts generally suitable for use herein are those selected from the group consisting of alkali metals, such as sodium, lithium and potassium; alloys of two or more alkali metals, such as sodium-lithium and sodium-potassium alloys; alkali metal hydrides, such as sodium, lithium and potassium hydride; and alkali metal alkoxides, such as potassium t-butoxide and sodium methoxide.

In the present invention, the basic catalyst used in the reaction is potassium carbonate, sodium carbonate, barium carbonate, or mixtures of these compounds. It has been found that when these specific compounds are used as the catalyst, shorter reaction times and/or increased yields of the higher polyol polyesters are obtained when compared to essentially identical reactions carried out using more conventional catalysts, such as sodium hydride, potassium hydride, soap, or sodium methoxide. These preferred catalysts may also be used in admixture with the more conventional basic catalysts, described above. Potassium carbonate is the most preferred catalyst for use herein.

In a preferred embodiment of this invention, the catalyst is dispersed in a suitable carrier so as to insure uniform distribution of the catalyst throughout the reaction mass. Suitable carriers or dispersing agents include, for example, methanol and fatty acid methyl esters.

In carrying out step 1, the above-described reactants are combined to form a heterogeneous mixture. The precise ratio of reactants can be freely selected from within the guidelines set forth hereinafter. However,

routine experimentation may be necessary in order to establish the optimum concentrations for a given set of reactants. In general, the heterogeneous mixture comprises from about 10% to about 50%, preferably from about 15% to about 30%, by weight of the polyol; from about 40% to about 80%, preferably from about 55% to about 75%, by weight of the fatty acid esters; from about 1% to about 30%, preferably from about 5% to about 20%, by weight of the alkali metal fatty acid soap; and about from about 0.05% to about 5%, preferably from about 0.1% to about 0.5%, by weight of the basic catalyst component.

It has surprisingly been found that when this mixture is formed so as to include relatively high molar ratios of soap:polyol, increased yields of the higher polyesters (e.g., the octaesters) are obtained when compared with similar reactions carried out using lower art-disclosed soap:polyol molar ratios (e.g., about 0.3–0.4:1). Specifically, these higher soap:polyol ratios result in increased yields of the higher polyols, more complete utilization of the polyol reaction component, and/or faster disappearance of free polyol from the reaction mixture. Soap:polyol molar ratios in step 1 of from about 0.6:1 to 1:1 are, therefore, preferred for use in the present invention. More preferred soap:polyol ratios fall in the range from about 0.75:1 to about 1:1, from about 0.75:1 to about 0.85:1, and most preferably about 0.75:1. The use of these high soap:polyol molar ratios is further disclosed and claimed in concurrently-filed patent application U.S. Ser. No. 507,826, Volpenhein, Synthesis of Higher Polyol Fatty Acid Polyesters Using High Soap:-Polyol Ratios, incorporated herein by reference.

The heterogeneous mixture is heated to a temperature within the range of from about 110° C. to about 180° C., preferably from about 130° C. to about 145° C., under a pressure of from about 0.1 mm to about 760 mm, preferably from about 0.5 mm to about 25 mm, of mercury. Within these temperature and pressure ranges, a homogeneous melt of partially esterified polyol and unreacted starting materials will form in from about 1 to 4 hours.

STEP 2

In the second step of the instant process, excess fatty acid methyl, 2-methoxy ethyl, or benzyl esters are added to the homogeneous melt formed in step 1. As used herein, the term "excess" is intended to include sufficient fatty acid esters to raise the overall ester: polyol mole ratio above about 8:1, preferably to about 12:1. Although ratios beyond 12:1 can be used, as a general rule, such ratios do not noticeably decrease reaction time or improve the yield and, therefore, tend to be impractical. When fatty acid methyl esters are used, it is preferred that after the excess ester is added to the reaction mixture, the mixture be heated to a temperature of from about 120° C. to about 160° C., preferably about 135° C., at a pressure from about 0.1 mm to about 10 mm, preferably from about 0.5 mm to about 2 mm, of mercury to form the polyol fatty acid polyester material. The reaction time for step 2 is preferably less than about 10 hours, and generally is between about 2 and 8 hours.

It should be noted that as the transesterification reaction proceeds, a lower alcohol is formed as a by-product. In order to promote the reaction, the alcohol by-product is preferably removed. Many removal techniques are known in the art, any one of which can be used to effectively and efficiently remove the lower alcohol. Vacuum removal both with and without an inert gas sparging has been found to promote the reaction. In any event, the formation of a lower alcohol presents no significant obstacle to the use of the process in the food or pharmaceutical industries.

The use of the preferred catalysts and soap:polyol ratios, defined herein, permit the combination of steps 1 and 2 into a single reaction step. In this single step approach, a mixture of (a) a polyol selected from monosaccharides, disaccharides and sugar alcohols; (b) an alkali metal fatty acid soap; (c) a basic catalyst selected from potassium carbonate, sodium carbonate and barium carbonate; and (d) an excess of fatty acid methyl, 2-methoxy ethyl or benzyl ester (wherein the soap:-polyol molar ratio is from about 0.6:1 to about 1:1, preferably from about 0.75:1 to about 1:1, more preferably from about 0.75:1 to about 0.85:1, most preferably about 0.75:1), is heated to a temperature of from about 100° C. to about 180° C. at a pressure of from about 0.1 mm to about 760 mm of mercury, thereby forming higher polyol fatty acid polyesters.

STEP 3

In the third step of the process, the polyol fatty acid polyesters formed in step 2 are separated from the reaction mix containing polyesters, soap, and unreacted starting materials. Separation can be accomplished by any of the separation procedures routinely used in the art. Distillation, water washing, conventional refining techniques or solvent extraction are preferred due to their simplicity and economy.

The following non-limiting examples are intended to further clarify the invention, but should not be construed as limiting thereof.

Each of the following reactions was carried out in a 1 liter 3-neck flask containing a stirrer, thermometer, reflux condensor, and vacuum outlet.

EXAMPLE I

Two Stage Reaction

Step (1): 3.6 g 85% KOH pellets (0.055 moles) dissolved in some methanol and 103 g (0.347 moles) soybean oil fatty acid methyl esters (FAME) were heated and stirred at reflux for two hours. 25 g sucrose (0.073 moles) and 1 g potassium carbonate were added and the condensor removed. The soap:sucrose molar ratio of the mixture was 0.75:1. The methanol was evaporated from the mixture under a gentle stream of nitrogen. When the reaction reached 100° C., a vacuum was applied and the temperature brought to 135° C. Conditions were maintained for two hours.

Step (2): 174 g additional FAME (0.585 moles) was drawn into the reactor. The final molar ratio of FAME to sucrose was 12:1. The temperature was allowed to recover to 135° C. and stirring under vacuum was continued for three hours. The vacuum slowly decreased in this time to from 5.0 to 0.5 mm Hg, as the methanol formed during the reactions was removed.

The reaction was cooled to 90°–100° C. and 200 ml 80:20:2 (by weight) water:alcohol:salt added and the mix stirred for 10 minutes at 80° C. The reaction mix was transferred to a separatory funnel and the phases allowed to separate. The lower aqueous soap solution was discarded and the lipid phase returned to the reactor for additional washes: first with a second 80:20:2 water:alcohol:salt wash and then with 2% aqueous acetic acid and two water washes (all at 80° C.). The

lipid was dried under vacuum, bleached with 1-5% Filtrol 105 (a bleaching earth), filtered and steam deodorized at 205° C. to remove excess FAME. The sample was weighed and the yield calculated as percent sucrose recovered as octaester.

The octaester content of the reaction product was determined by separating the mix on a silica gel column and weighing the relative amount of octaester and partial esters recovered. The product formed comprised a mixture of the higher polyesters of sucrose, having a high octaester content.

Substantially similar results are obtained when the potassium carbonate catalyst is replaced, in whole or in part, by sodium carbonate, barium carbonate or mixtures thereof. Similar results are also obtained when the sucrose is replaced, in whole or in part, by sorbitol, xylitol, mannitol or galactitol. The FAME is replaced, in whole or in part, with soybean oil benzyl esters, soybean oil 2-methoxy ethyl esters or the methyl esters of palm oil, sunflower oil, safflower oil, or corn oil; similar results are obtained. Similar results are also obtained when the potassium soybean oil fatty acid soaps used in the above example are replaced, in whole or in part, by the lithium, sodium, rubidium or cesium salts of fatty acids derived from sunflower oil, safflower oil or corn oil.

EXAMPLE II

Single Stage Reaction

3.6 g 85% KOH pellets (0.055 moles) dissolved in 50 ml methanol and 278 g (0.933 moles) soybean oil fatty acid methyl esters were refluxed for two hours. 25 g (0.073 moles) sucrose and 1 g potassium carbonate were added. The soap:sucrose molar ratio of the mixture was 0.75:1. The methanol was evaporated from the mixture under nitrogen. When the reaction reached 100° C., a vacuum was applied and the temperature raised to 135° C. Reaction conditions were maintained for four hours. The reaction was cooled, 15 ml. of water added, stirred 5 minutes and certrifuged (45 minutes, 8000 RPM). The mixture of higher sucrose polyesters was then decanted from the soap. The mixture was then bleached with 1-5% Filtrol 105, filtered and steam deodorized at 205° C. to remove excess FAME.

The product formed comprised a mixture of the higher polyesters of sucrose, having a high (about 85%) octaester content.

Substantially similar results are obtained when the potassium carbonate catalyst is replaced, in whole or in part, by sodium carbonate or barium carbonate. Similar results are also obtained when the sucrose is replaced, in whole or in part, by sorbitol, xylitol, mannitol or galactitol. The FAME is replaced, in whole or in part, with soybean oil benzyl esters, soybean oil 2-methoxy ethyl esters or the methyl esters of palm oil, sunflower oil, safflower oil, or corn oil; similar results are obtained Similar results are also obtained when the potassium soybean oil fatty acid soaps used in the above example are replaced, in whole or in part, by the lithium, sodium, rubidium or cesium salts of fatty acids derived from sunflower oil, safflower oil or corn oil.

EXAMPLE III

The general procedure described in Example I was used to compare the effectiveness of various catalysts. Those tested included potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3), sodium methoxide (NaOMe), sodium hydride (Na.H) and potassium hydroxide (KOH), all at 10 mole percent of the sucrose in the reaction. K_2CO_3, NaOMe, and potassium hydride (K.H) were also compared at four weight percent of the sucrose. The results are summarized in the table below.

Effect of Various Catalysts on the Synthesis of Sucrose Polyesters

Catalyst	Concentration (Sucrose Basis)	% Yield	% Octa-Ester
K_2CO_3	10 mole %	90	75
Na.H	10 mole %	76	36
NaOMe	10 mole %	85	63
KOH	10 mole %	58	Not determined
Na_2CO_3	10 mole %	79	40
None	—	45	5
K_2CO_3	4 weight %	92	79
NaOMe	4 weight %	79	79
K.H	4 weight %	80	80

EXAMPLE IV

To assess the effect of soap level on the reaction, the reaction as described in Example I was utilized. The concentration of soap in the reaction mix was controlled by either varying the amount of KOH added at the beginning or by adding varying amounts of preformed potassium soaps.

Two analytical methods were used to monitor the effect of soap on the reaction. In the first, varying amounts of KOH and radiolabelled sucrose were used. At the end of the first two hours, before the second addition of FAME, the reaction was stopped and partitioned between hot water and ethyl acetate. The amount of ^{14}C activity found in the water relative to that added as free sucrose at the beginning of the reaction was a measure of unreacted sucrose. These results are summarized below.

Effect of Soap Concentration On Sucrose Reaction

Grams KOH Added	Molar Ratio Soap:Sucrose	Unreacted Sucrose Remaining after 2 hrs.
3.6	0.75	1.2
2.4	0.5	3.6
1.4	0.3	14.0
0	0	100

In the second test, varying amounts of preformed potassium soap were added to the mixture in place of KOH. The effect of the soap was judged by measuring yield of sucrose polyesters and octaester content. The results obtained are as follows.

Effect of Soap Concentration On Yield of Sucrose Polyester

Grams Potassium Soap Added	Molar Ratio Soap:Sucrose	% Yield	% Octaester
4.7	0.2	Foamed & charred too badly during reaction to recover	
7.7	0.33	75	47
15.0	0.64	90	80
17.6	0.75	93	77
23.5	1.0	91	74

What is claimed is:

1. In a solvent-free transesterification process for synthesizing higher polyol fatty acid polyesters comprising the steps of:

(1) heating a mixture of (a) a polyol selected from a group consisting of monosaccharides, disaccharides and sugar alcohols, (b) a fatty acid ester selected from the group consisting of methyl esters, 2-methoxy ethyl esters, benzyl esters, and mixtures thereof, (c) an alkali metal fatty acid soap, and (d) a basic catalyst, to a temperature of from about 110° C. to about 180° C. at a pressure of from about 0.1 mm of mercury to about 760 mm of mercury to form a homogeneous melt; and

(2) subsequently adding to the reaction product of step (1) excess fatty acid ester selected from the group consisting of methyl esters, 2-methoxy ethyl esters, benzyl esters and mixtures thereof;

the improvement wherein the basic catalyst is potassium carbonate.

2. The process according to claim 1 wherein the polyol is a disaccharide.

3. The process according to claim 1 wherein the polyol is selected from the group consisting of sucrose, xylitol, sorbitol, and mixtures thereof.

4. The process according to claim 1 wherein the fatty acid esters are fatty acid methyl esters.

5. The process according to claim 4 wherein the methyl esters are derived from materials selected from the group consisting of soybean oil, sunflower oil, palm oil, safflower oil, corn oil, and mixtures thereof.

6. The process according to claim 1 wherein the mixture of step (1) is heated to a temperature from about 130° C. to about 145° C.

7. The process according to claim 1 wherein the molar ratio of soap:polyol in step (1) is from about 0.6:1 to about 1:1.

8. The process according to claim 7 wherein the molar ratio of soap:polyol in step (1) is from about 0.75:1 to about 1:1.

9. The process according to claim 1 wherein the reaction mixture of step (1) comprises from about 10% to about 50% by weight of the polyol, from about 40% to about 80% by weight of the fatty acid esters, from about 1% to about 30% by weight of the alkali metal fatty acid soap, and from about 0.05% to about 5% by weight of the basic catalyst.

10. The process according to claim 9 wherein the polyol is sucrose.

11. The process according to claim 10 wherein the fatty acid ester is a fatty acid methyl ester.

12. The process according to claim 11 wherein the methyl ester is derived from a material selected from the group consisting of soybean oil, sunflower oil, palm oil, safflower oil, corn oil, and mixtures thereof.

13. The process according to claim 12 wherein the mixture of step (1) is heated to a temperature of from about 130° C. to about 145° C.

14. The process according to claim 13 wherein the molar ratio of soap:polyol in step (1) is from about 0.75:1 to about 1:1.

15. The process according to claim 14 wherein after the addition of the ester in step (2), the reaction mixture is heated to a temperature of from about 120° C. to about 160° C. at a pressure of from about 0.1 mm to about 10 mm of mercury to form the polyol fatty acid polyesters.

16. The process according to claim 9 wherein water is added to the mixture of step (2), said mixture is centrifuged and the higher polyol fatty acid polyesters are separated therefrom.

17. A single-step solvent-free transesterification process for synthesizing higher polyol fatty acid polyesters, comprising the heating of a mixture of:

(a) a polyol selected from the group consisting of monosaccharides, disaccharides and sugar alcohols;

(b) an excess amount of fatty acid esters selected from the group consisting of methyl esters, 2-methoxy ethyl esters, benzyl esters, and mixtures thereof;

(c) an alkali metal fatty acid soap; and

(d) a catalytic amount of potassium carbonate;

wherein the molar ratio of soap:polyol in said mixture is from about 0.75:1 to about 1:1;

to a temperature of from about 110° C. to about 180° C. at a pressure of from about 0.1 mm to about 760 mm of mercury.

* * * * *

(B)

INTERDEPARTMENTAL CORRESPONDENCE

From: S.D. Pearson/G.R. Wyness

Date: March 22, 1989
REVISED MARCH 28

To: Distribution

Retention Limit: 03/1/90

Subject: P90327 ExperimentalTest Plan - Fryma Milling Test

OBJECTIVE

The objective for this run is to examine the effects of milled sucrose on the continuos reaction, and to test different modes of milling. Completion of these experiments will help us understand what the sucrose particle size requirements are for the Test Market with the current process, and where the best place in the process to locate the mill is.

Experimental

The run consists of three experiments. In the **first**, sucrose/ester slurry will be milled (without soap). In the **second**, sucrose will be milled in our normal procedure, i.e., in the presence of soap and in a single pass thru the mill. In the **third**, the sucrose will be milled to a greater than normal degree by recirculating thru the mill for 2.5 hours.
Changeovers between tests will be simply clean breaks, we will not dump and restart the first two reactors.

We will use all the reactors through 607 for all runs. Operating conditions will be the same for all runs. As in the past, the catalyst injection system will be used to add all the powdered carbonate, and two reactors are planned for stage I (R600 & R601). The experimental conditions are shown below. (See Experimental Conditions Checklist for complete details).

Pressure (mm Hg)	
Stage I	15
Stage II	2
Stage III	2
Catalyst cycle (minutes):	
R600	11
R601	15
R602	7
R603	7
Feedrate Sucrose/ester (lb/hr)	55/66

Stage II ester addition will be evenly split between R601 & R602.

Two feed batches are required.
The first feed batch will be made as follows: A 30% sucrose in ester slurry will be made in 001, using 800# sucrose, 1,870# ester. It will be transferred to 026 thru the mill. Soap made in 501 will be transferred to 001 while the MeOH is evaporated. Chase with 250# ester, add 1080# cool ester, transfer to 026. This is feed for run 1.
While run 1 is proceeding, prepare a second feed batch in 001 (soap from 501) following Semi-Works procedures.. When run 1 is complete, stop the reaction system (lower temperature to 260F, reduce vacuum), empty 026. Then transfer approximately half the feed batch from 001 to 026 thru the mill to 026. Restart feed to the reaction system from 026. This is run 2. Approximately 3-4 hours before 026 runs empty start recycle milling of 001. This milling should be done for 2.5 hours. When run 2 ends, blow the slurry recirculation line, then start run 3 by feeding from 001.

1. **It is critical that the experimental conditions be closely monitored and adhered to.** Please clear all significant deviations from the run plan through me first.

2. Detailed analysis schedules will be posted in the lab. SAMPLES MUST BE TAKEN FROM EVERY ESTER BLEND.

3. The data should be plotted on a control chart. One person on each shift will be responsible for this.

PROPOSED TIMETABLE

		Cumulative Time (hr)	Event
		0	R600 start-up, feed from 026, use two shots from injector initially, once through foaming turn on injector as reactor is filled.
		8	R600 through foaming and full, **run 1**, feed to drum
		9	feed to R601 and add 1/2 of second stage esters while filling
		11	R601 full, feed to drum
		12	feed to R602 and start adding remaining 1/2 of 2nd stage esters to 601 while filling
		14	R602 full. feed to R603 and continue to fill to R607..
3/28	20:00 ✓	~~22~~ 14	all reactors full and feeding forward
03/29	14:00	~~40~~ 33	**run 1** complete, stop reaction system, clear 026, mill 1/2 feed batch from 001 to 026. clear slurry recirculation line
3/29	16:00	~~42~~ 43	start **run 2** by feeding from 026
3/30	16:00	~~56~~ 59	**run 2** complete, clear slurry recirc line, change over to 001 start **run 3**
3/31	16:00	~~90~~ 83	**run 3** complete.

Materials:

All feed vessels should be drop tested prior to use. Two sucrose feed batches are necessary, prepared in the following manner:

Batch 1:
1. Charge 1870# ester to 001.
2. Add 800# sucrose to 001.
3. Agitate for 15 minutes then transfer to 026 through the mill, chase with 250# ester.
4. Make soap in 501., following Semi-Works procedures.
5. Pump 1000# of stage I esters into 001.
6. Transfer soap solution from 501 to 001 while evaporating methanol; chase with 250# ester blend
7. Pump 330# of stage I esters into 001 from truck, cool batch to 180F if necessary..
8. Transfer soap/ester mixture to 026.

Batch 2:
1. Make a normal batch in 001 following Semi-Works procedures,(use fresh MeOH), add 2,450# cool esters but no 250# chase thru the mill) but do not recirculate through the mill; clear 026, then transfer 1/2 the batch through the mill to 026.
2. Feed from 026 for run 2
3. Feed from 001 for run 3.

Prior to starting up R600, pull a vacuum on sucrose feed (and for subsequent feed batches before they are used) and on second stage esters for 10 minutes. Moistures should be run on sucrose and second stage ester feed every 4 hours and before a new feed batch is brought on stream. Maintain 008, 001, 026 and the catalyst slurry tank under N_2 throughout the run.

The amount of material, following methanol evaporation, is:

Component	Wt per Batch
Sucrose	800
KOH	100
I-1 (soap)	550
Ester	3700
	5150
Methanol requirements	1100

One catalyst batch is necessary, prepared in 3243 as outlined in the Semi-Works procedures. The amount of material is:

Component	Wt per Batch
powdered K2CO3	300
Ester	900
	1200

The following is a breakdown of ester requirements for the entire run:

Component	Wt
Feed batches	7,400
Direct ester feed	5,300
Catalyst	900
Total	13,600

S.D. Pearson/G.R. Wyness

Distribution
S.R. Alexander
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(14)

INTERDEPARTMENTAL CORRESPONDENCE

FROM: S. D Pearson DATE: July 14 1989

TO: Distribution RETENTION LIMIT: 7/1/90

SUBJECT: P90327 RUN SUMMARY

SUMMARY

The objective for the three experiments of P90327 was to evaluate the effects different modes of wet milling the sucrose slurry may have on the FG reaction. The three modes of milling were: the normal procedure of once thru the mill with soap (16% sucrose), once thru the mill without soap (30% sucrose), and milled to a greater than normal degree by recirculating thru the mill for 2.5 hours (approximately five turnovers of a 16% sucrose slurry). These tests further our understanding of what the sucrose particle size requirements are for the continuous process and verify the mill location chosen for Test Market. Blend Y' esters (47% I85/53% hardstock) were used. Standard reactor conditions were used including a stage I pressure of 15 mmHg and stage II & III pressure of 2.0 mmHg.

P90327 lasted for 83 hrs and accomplished the milling evaluation. Good steady-state results for the process parameters were obtained and the final octaester ranged from 89% for the feed milled once thru with soap to 96% for the recycle milled feed. Image analysis of the feed batches indicates the three milling methods gave different sucrose particle sizes which influenced stage I results and may have ultimately affected final conversion. The successful test of milling without soap confirmed the Test Market plan of locating the Fryma mill in the main sucrose recirculation line.

KEY POINTS

1. The Fryma mill again performed very well. There were no mechanical problems associated with the mill during the run. Operationally, however, the gap setting appears to wander while the mill is being cleaned for subsequent feed batches. We need to develop a more refined way of setting the gap and *locking* in the current setting so it cannot be changed. The mill gap sets the sucrose particle size which profoundly influences the reaction characteristics, and so must be tightly controlled.

2. The mode in which the feed is milled affects the sucrose particle size; smaller sucrose particle sizes improve utilization and may increase final conversion. The sucrose size (number average basis) using image analysis varied from approximately 21 μ for once thru with soap to 16 μ for the recycle milled condition. The larger size sucrose, probably due to its lower specific suface area , was not utilized as effectively in stage I. Sucrose concentration from stage I was only 0.37% when the feed was recycle milled while it was 0.98% for the once thru with soap test. The milling mode was also evident late in the reation where, for example, the recycle milled batch reached the highest conversion of 96% octaester. It is unclear why residual sucrose can affect final conversion, more experiments are planned to further elucidate this relationship.

3. Locating the mill on the sucrose recirculation line for Test Market is appropriate. The three different milling modes tested in P90327 were chosen based on possible Test Market locations. From a process control point of view the sucrose recirculation line installation is preferred. Results from this series of experiments suggest that milling without soap, as would be the case for this location, presents no process problems.

CHRONOLOGY

Cumulative Time (hr)	Event
0	R600 through foaming and full, feed to drum for 1 hr, begin run 1 (milled once thru without soap at 30% sucrose)
1	feed to R601 and added 1/2 of 2nd stage esters while filling
2.3	R601 full, feed to drum for 1 hr.
3.3	feed to R602 and added remaining 1/2 of 2nd stage esters to 602 while filling
4.7	R602 full, feed to R603 and continued to fill to R606
14	all reactors full and feeding forward
26	slurry feed pump went out
26.5	system temporarily shut down while pump is being fixed by shuting off catalyst, N_2 sparge, 2nd stage esters and closing header.
27	slurry feed pump repaired, system brought back up
28.5	R600 & R601 catalyst injectors started cycling rapidly, R601 injector shut off to allow catalyst level in R601 to drop.
30.6	restarted R601 catalyst injector.
33	run 1 complete, stop reaction system, clear 026, mill 1/2 of 2nd feed batch from 001 to 026.
35	start run 2 (milled once thru with soap at 16% sucrose) feeding from 026.
56	start recycle milling 2nd sucrose slurry batch in 001
58.5	end recycle milling in 001
59	run 2 complete, clear slurry recirculation line, change over to 001 and start run 3 (recirculating thru the mill for 2.5 hours)
83	run 3 complete.

OPERATIONAL DETAILS

A. FEED STREAMS

Straight Blend Y' esters (R90302) were used for P90327; no hardstock was added. Carbonyl levels were measured at 50 ppm. Moisture was less than 0.1% for the entire run. Two milled sucrose batches and one powdered K_2CO_3 feed batch were necessary.

The catalyst batch (25% K_2CO_3) was prepared in 3243 and transferred to the catalyst slurry feed tank as required. During the course of the run 3243 was kept under a N_2 blanket. Cycle times for the injectors were 11/15/7/7 min for R600-R603 repectively.

Soap for the sucrose feed batches were made in 501 following the Semi-Works procedures then transferred to 001 for methanol removal. Residual base was measured at 0.11% and 0.15% for the two soap batches made.

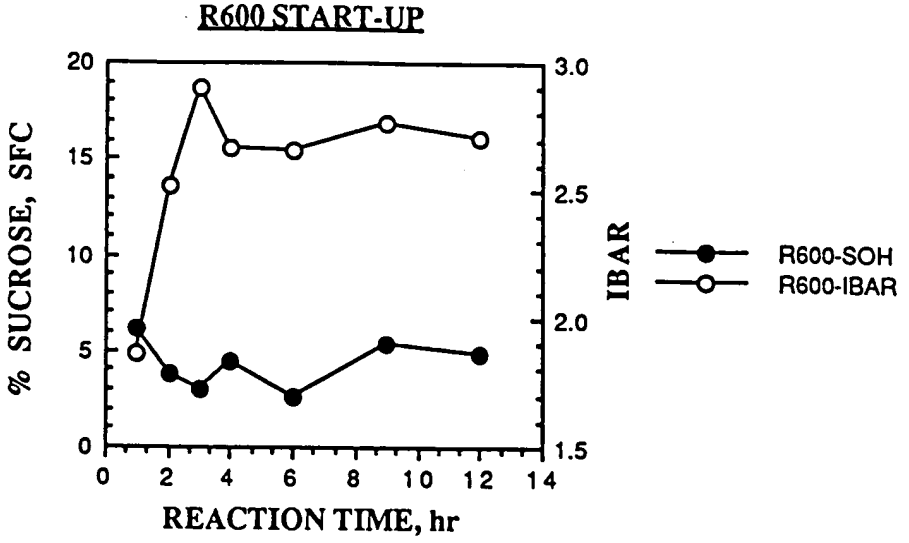
Two sucrose feed batches were required. In the first batch, the sucrose (30%) was milled once thru to 026 before the soap and the rest of the stage I esters were added. For the second feed batch the normal 70# procedures were followed until the milling step. At this point half the batch was milled over to 026 (which had been cleaned of feed from run 1) while the remainder was recirculated thru the mill and back into 001 for 2.5 hrs. Approximately 5 turnovers of the feed occured during the recycle milling. Run 2 was fed from 026 using the normal once thru the mill with soap (16% sucrose) feed and Run 3 was fed from 001 with the recycle milled feed. The Fryma mill gap was nominally set at 1/4 turn off stop and the pump on 001 was set at 30%. The feed vessels were kept under N_2 blanket during the run. Moisture levels in the sucrose feeds remained under 0.1% throughout the run.

Stage II esters were fed from 008 for all three runs. Esters were dried and sampled each time they were brought in from the truck.

B. START-UP, R600

The stage I start-up procedure was slightly modified for this run to test an alternative filling condition following initial foaming. Initial foaming was typical; foaming started roughly 30 min after reaching 270°F and lasted for 40 min. At this point the normal procedure is to fill slowly while at full vacuum until secondary foaming subsides. We attempted to fill at full feedrate and at the stage I pressure of 15 mmHg to better understand the start-up limitations. Under these modified conditions secondary foaming started almost immediately after feed was started into R600 and did not subside for two hours. It was clear that the secondary foaming was uncontrollable using this procedure so the level in R600 was dropped back to 0.5 in. and filling was resumed, this time at full vacuum and full rate. Secondary foaming was easily controlled under these filling conditions and when the level reached 3 in. the pressure was brought up to the desired reactor condition of 15 mmHg. Filling R600 while at full vacuum appears to be essential until secondary foaming has subsided.

The figure below illustrates the good start-up behavior of R600 to the feed milled without soap at a sucrose concentration of 30%. Time 0 corresponds to the R600 being full and feeding forward either to a drum or to R601. Steady-state is reached in three residence times (4.5 hr); no unusual characteristics attributable to the feed being milled without soap are apparent. This was an important demonstration for the Test Market scenario where the



Fryma mill will be located in the sucrose recirculation line and milling will occur without soap. Based on the above test, there should be no start-up problems associated with no soap milling.

The reliability of the slurry feed pump continues to be a problem. At 26 hrs into the run the tubing failed even though it had been rebuilt prior to the start of the run. While the pump was being repaired the reactor train was shut down in the following manner:

1. Catalyst injectors turned off to R600-R603
2. Stage II ester turned off to R601 and R602
3. N_2 sparge in R603-R607
4. Close vacuum headers in R600-R607

In addition, the reactor temperatures were closely monitored to prevent overshoots. If the shutdown had been for an extended period of time (more than 1 hr) the reactor temperatures would also have been lowered. This procedure worked very well and the reactors were quickly brought back on-line after the slurry feed had been reestablished.

C. Reactors R601-R607

Reactors R601 thru R606 performed mechanically quite well during this run. The standard operating conditions of 15 mmHg in stage I and 2 mmHg in stage II were used. A full listing of operating conditions for each reactor is in the Appendix.

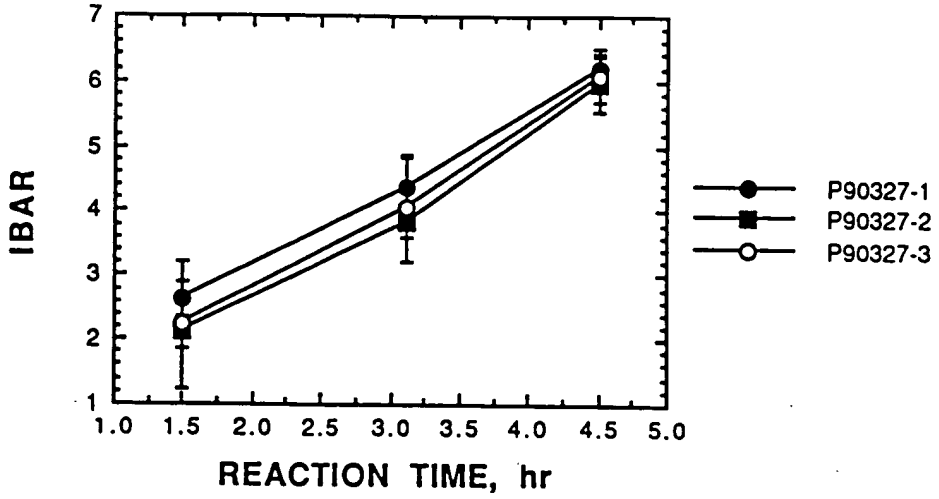
Reactor R607 was repaired prior to the start of the run, allowing us to use an eight reactor train. Temperature control of R607 was difficult due to a bad regulator. Course control was achieved by opening and closing the bleeder valve on the reactor jacket.

The #1 or #2 vacuum systems were used for reactors R602-607 depending on whether or not the methanol removal step was taking place during preparation of the second feed batch.

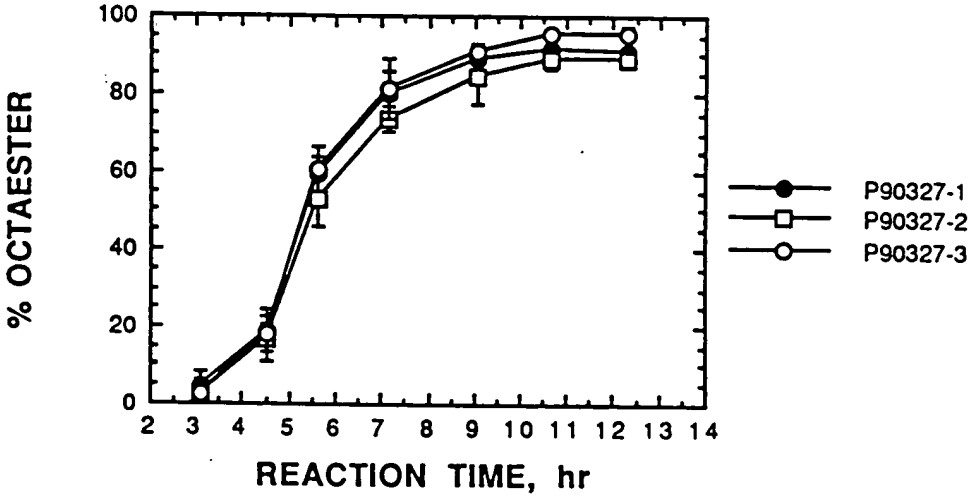
RESULTS AND DISCUSSION

A.

STEADY-STATE IBAR PROFILE



STEADY-STATE OCTAESTER PROFILE



(15)

INTERDEPARTMENTAL CORRESPONDENCE

From: S. D. Pearson

Date: April 20, 1989

To: Distribution

Retention Limit: 04/1/90

Subject: **P90424 Experimental Test Plan**

This memo summarizes the run plan for the upcoming 70# run scheduled for the weeks of April 24 and May 1.

OBJECTIVE

The objective for this run is to examine the effects of various particle sizes of milled sucrose on the continuous reaction, and to test the effects of temperature in stage II & III. Completion of the these experiments during the P90424 run will help us understand what the sucrose particle size requirements are for Test Market with the current process.

EXPERIMENTAL

The run consists of six experiments. The first run in divided into four parts in order to evaluate stage I conditions for sucrose utilization at a given feed particle size. Two of these stage I conditions (as determined by PDD) will be run out so that the entire train will reach steady-state in order to assess final conversion. For this first run the sucrose feed batch will be recycle milled, without soap, at a concentration of 30% for 90min. Two additional feed batches will be prepared and milled so that three additional particle sizes can be evaluated (unmilled, once-thru with soap, and recycle milled for 5 hrs with soap) in full length runs This will let us understand particle size effects on stage I utilization and ultimately on final conversion. Two full runs will also examine the influence of different temperatures (285°F, and 265°F) in stage II & III.

We will use all the reactors through 607 for all the conditions. As in the past, the catalyst injection system will be used to add all the carbonate and two reactors are planned for stage I (R600 & R601).. Stage II ester addition will be evenly split between R601 & R602. Blend Y esters will be used for this run. The experimental conditions are shown in the Experimental Conditions Checklist.

1. It is critical that the experimental conditions be closely monitored and adhered to. Please clear all significant deviations from the run plan through me first.

2. Detailed analysis schedules will be posted in the lab. SAMPLES MUST BE TAKEN FROM EVERY ESTER BLEND. WRITE IN LOGBOOK WHENEVER ADDITIONS ARE MADE TO THE CATALYST TANK.

3. The data should be plotted on a control chart. One person on each shift will be responsible for this.

PROPOSED TIMETABLE

Cumulative Time (hr)	Event
0	R600 start-up, feed from 026, use two charges from injector initially, once through foaming turn on injector as reactor is filled
8	R600 through foaming and full, **run 1**, feed to drum
9	feed to R601 and add 1/2 of 2nd stage esters while filling
11	R601 full, feed to drum
12	feed to R602 and start adding remaining 1/2 of 2nd stage esters to 601 while filling
14	R602 full, feed to R603 and continue to fill to R607
22	all reactors full and feeding forward
37	**run 1A** complete, start **run 1B**
38	start 2nd sucrose feed batch preparation, following sucrose addition mill in recycle mode for 5 hrs
TBD	**run 1B** complete, start **run 1C**
TBD	**run 1C** complete, start **run 1D**
89	**run 1D** complete, change slurry pump, stop reaction system, clear slurry recirculation line, start **run 2** by feeding from 001
113	**run 2** complete, shut down for weekend, dump R600, clear slurry recirculation line, transfer feed batch to 026
**	weekend shutdown
0	R600 start-up, feed from 026, use 2nd catalyst batch, use two charges from injector initially, once through foaming turn on injector as reactor is filled
8	R600 through foaming and full, **run 3**, feed to drum for 1 hr
9	feed to R601 and add 1/2 of 2nd stage esters while filling and continue to fill to R607
22	all reactors full and feeding forward
37	**run 3** complete, start **run 4**
38	start 3rd sucrose feed batch preparation
61	**run 4** complete, stop reaction system, clear 026, mill 1/2 feed batch from 001 to 026, clear recirculation line, start **run 5** by feeding from 001
85	**run 5** complete, clear slurry recirculation line, change over to 026 start **run 6**
109	**run 6** complete

MATERIALS

All feed vessels should be drop tested prior to use. three sucrose feed batches are necessary, the soap batches should be prepared using the procedures developed for Semi-Works (i.e. using 501 and removing MeOH in the PHX in the 001 recirculation line). Do not, however, recycle MeOH for subsequent soap batches, use dry MeOH.

Batch 1:

1. Charge 1870# ester to 001

2. Add 800# sucrose
3. Agitate for 15 min then recycle mill back into 001 for 90 min
4. Transfer to 026, chase with 250# ester
5. Make soap in 501 following Semi-Works procedures
6. Transfer soap solution from 501 to 001 while evaporating MeOH, chase with 250# ester
7. Pump remaining 330# of stage I esters into 001, cool to 180°F if necessary
8. Transfer soap/ester mixture to 026

Batch 2:

1. Make a normal batch in 001 following Semi-Works procedures (use fresh MeOH, no mill chaser), cool with 2450#esters
2. Add sucrose and recirculate thru mill and back into 001 for 90 min
3. Feed run 2 from 001
4. Transfer remainder of Batch 2 to 026 (cleaned out) at start of week 2 and feed runs 3 and 4 from 026

Batch 3:

1. Make a normal batch in 001 following Semi-Works procedures (use fresh MeOH no mill chaser), cool with 2450#esters
2. Add sucrose, clear 026, then transfer 1/2 the batch thru the mill to 026
3. Feed from 001 for run 5
4. Feed from 026 for run 6

Prior to starting up R600, pull a vacuum on sucrose feed (and subsequent feed batches before use) and second stage esters for 10 min. Moistures should be run on sucrose and second stage ester feed every 6 hours and before a new feed batch is brought on stream.Maintain 008, 001, 026, and the catalyst slurry tank 3243 under N2 throughout the course of the run. The amount of material, following methanol evaporation, is:

Component	Wt per Batch
Sucrose	800
KOH	100
I-I (soap)	550
Ester	3700
	5150
Methanol requirements	1100

Two catalyst batches are necessary, prepared in 3243, as out-lined in the Semi-Works procedures. The batches should be prepared at the start of each week. The amount of material is:

Component	Wt per Batch
powdered K2CO3	288
Ester	864
	1152

The following is a breakdown of ester requirements for the entire run:

Component	Wt
Stg I	11,100
Stg II	14,600
Catalyst	1728

S. D. Pearson

Distribution
S. R. Alexander
R. J. Belanger
D. J. Bruno
D. D. Farris
R. G. Fencl
B. P. Grady
J. K. Howie
R. Sarama
S. VanDiest
V. Wee
G. R. Wyness
✓Bldg 96 via C. White

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INDUSTRIAL CHEMICALS PRODUCT DEVELOPMENT BIWEEKLY REPORT

S. D. PEARSON

PERIOD ENDING MAY 31, 1989

Pilot plant run P90424 yielded significant new learnings regarding sucrose particle size, temperature, and reduced soap effects on the continuous FG reaction.

FG REACTION TECHNOLOGY

In the last pilot plant run, P90424, we performed a series of experiments to examine the effects of milled sucrose particle size, different temperatures in stage II & III, and reduced levels of soap in the feed. The continuous system again performed quite well during this two week period, allowing us to meet all the experimental objectives. Some of the conclusions that can be drawn from the data include the following:

1) Wet milling of the sucrose is effective in reducing the particle size sufficiently to achieve 98% octaester. By comparison, an unmilled sucrose feed batch reached only 93% octaester. The reason for these results seems to be related to sucrose utilization in stage I and the amount of sucrose present late in the reaction. The milled sucrose was more available for esterification in stage I because of its relatively larger specific surface area, which means less is around late in the reaction, yielding a high conversion. At this point, however, we don't know the mechanism by which free sucrose influences final conversion, i.e., whether it is an equilibrium effect or simply being brought in late.

2) Lower temperatures (265°F or less) are desirable both from an increased conversion and reduction in burnt sucrose view. At 285°F in stage II & III (10°F above our normal operating condition) the apparent reaction rate was significantly faster than at 265°F but conversion plateaued in the low 90% octa range, while the lower temperature condition reached 99+% octaester. In addition, there was no observable burnt sucrose at the lower temperature. These results are consistent with lab batch experiments conducted by Nelson Holzschuh a few months ago. From the data (and recent work by J. Kao) it is clear that even lower temperatures are possible which may translate into significant color improvements.

3) Reduced soap processing is feasible without compromising final conversion. We were able to reach high octaester content at half the soap level in the feed. Being able to run at reduced soap levels plays out as a substantial economic benefit on larger scale systems. The effect of less soap in the reaction was to apparently reduce sucrose solubility in stage I resulting in slower reaction rates and poorer utilization. There was a downside to lower soap processing, i.e. mechanical problems such as plugging of heat exchangers were experienced. This may just be a problem at the pilot plant scale, however, we will examine it in the future.

The next pilot plant run scheduled for early June will continue to examine main effects, in particular we will attempt a no-soap experiment as well as operating at temperatures as low as 245°F. This will give us further insight into the reaction and allow us to explore different operating areas and assess their impact on color and DFK formation.

S. D. Pearson

SDP/elg/2015

Keywords: continuous reaction, temperature, soap, particle size

(17)

INTERDEPARTMENTAL CORRESPONDENCE

From: S. D. Pearson

Date: June 2, 1989

To: Distribution

Retention Limit: 05/1/90

Subject: **P90605 Experimental Test Plan**

This memo summarizes the run plan for the upcoming 70# run scheduled for the weeks of June 5 and 12.

OBJECTIVE

The objectives for this run are to continue to examine main effects on the continuous reaction. In particular we will test reduced soap levels, lower temperatures in stage II & III, and higher feed rates. Blend Y esters will be used for this run.

EXPERIMENTAL

The run consists of three main effects experiments, totalling eight different reaction conditions. In the first set of three conditions we will evaluate reduced soap levels in the feed. Soap levels of 50%, 25% and 0% of normal will be tested. The first sucrose (all three batches required for P90605 need to be recycle milled for 5 hrs) and soap feed batch will be partitioned between the three conditions as directed by PDD to achieve the required compositions. Stage I pressure for the entire run will be 25 mmHg and stage II & III pressure will be 2.0 mmHg. It is critical that conditions be closely monitored in the reduced soap run. The recirculation loops may need to be opened frequently to avoid clogging problems.

Following the soap experiments, the second effect to be evaluated is higher feed rates; the second feed batch will be used for this set. We would like to get up to at least 82 lb/hr (1.5X) for the slurry feed rate and have all the reactors lined out. The maximum rate will, of course, be determined by the system capability, which is what we are trying to evaluate. The characteristic of most interested is reaction rate, not necessarily extent.

The last set of conditions will be directed at extending our understanding of lower temperature operation. Stage II & III temperatures of 260°F and 245°F will be tested.

We will use all the reactors through 607 for all the conditions. As in the past, the catalyst injection system will be used to add all the carbonate and two reactors are planned for stage I (R600 & R601).. Stage II ester addition will be evenly split between R601 & R602. Blend Y esters will be used for this run. The experimental conditions are shown in the Experimental Conditions Checklist.

1. It is critical that the experimental conditions be closely monitored and adhered to; clear all significant deviations from the run plan through me first.

2. Detailed analysis schedules will be posted in the lab. SAMPLES MUST BE TAKEN FROM EVERY ESTER BLEND. WRITE IN LOGBOOK WHENEVER ADDITIONS ARE MADE TO THE SMALL CATALYST TANK.

3. The data should be plotted on a control chart **as it is taken.** One person on each shift will be responsible for this.

PROPOSED TIMETABLE

Cumulative Time (hr)	Event
0	R600 start-up, feed from 026 at 55 lb/hr for 20 min to get heel, use two charges from injector initially, once through foaming fill at reduced rate until level reaches 3 in then fill at full rate turn on injector as reactor is filled
8	R600 through foaming and full, **run 1**, feed to drum
9	feed to R601 and add 1/2 of 2nd stage esters while filling
11	R601 full, feed to drum
12	feed to R602 and start adding remaining 1/2 of 2nd stage esters to 602 while filling
14	R602 full, feed to R603 and continue to fill to R607
22	all reactors full and feeding forward
37	**run 1A** complete, start **run 1B** feeding from 001
61	**run 1B** complete,start **run 1C**
38	start 2nd sucrose feed batch preparation, following sucrose addition mill in recycle mode for 5 hrs
85	**run 1C** complete, shut down for weekend, dump &rinse reactors, change tubing pump
**	**weekend shutdown**
0	R600 start-up, feed from 026 at 55 lb/hr for 20 min to get heel, use two charges from injector initially, once through foaming fill at reduced rate until level reaches 3 in then fill at 1.5X full rate turn on injector as reactor is filled
8	R600 through foaming and full, **run 2A**, feed to drum
9	feed to R601 and add 1/2 of 2nd stage esters while filling (@ 1.5X rate)
11	R601 full, feed to drum
12	feed to R602 and start adding remaining 1/2 of 2nd stage (@ 1.5X rate) esters to 602 while filling
13	R602 full, feed to R603 and continue to fill to R607
19	all reactors full and feeding forward
27	**run 2A** complete, start **run 2B**
28	start 3rd sucrose feed batch preparation
44	**run 2B** complete, clear recirculation line, start **run 3A** by feeding from 001
68	**run 3B** complete, start **run 3C**
92	**run 3B** complete,change tubing pump, start **run 3C**
116	**run 3C** complete

MATERIALS

All feed vessels should be drop tested prior to use. Three sucrose feed batches are necessary, the soap batches should be prepared using the procedures developed for Semi-Works (i.e. using 501 and removing MeOH in the PHX in the 001 recirculation.line). Do not, however, recycle MeOH for subsequent soap batches, use dry MeOH.

Batch 1:

1. Make a normal soap batch in 501 and follow Semi-Works procedures thru MeOH removal in 001. **Do not cool with esters**, use heat exchanger to cool < 200°F.
2. Transfer 300# (1/6) of soap batch to 026 and the remainder to 501, both should be agitated and under N2
3. Rinse 001 to remove residual soap.
4. Add 2450 lb of esters to 001.
5. Add 800 lb sucrose and recirculate thru mill and back into 001 for 5hrs

For **run 1A**:

6. Transfer 1100# (1/3) of sucrose slurry to 026
7. Add 210 # of Blend Y esters to 026
8. Pull sample from 026 & measure soap and sucrose levels, adjust as needed for **run 1A**
9. Feed run 1A from 026

For **runs 1B & 1C**:

10. Empty and rinse 026, then transfer 150# of soap from 501 to 026 and 1100 # of sucrose slurry from 001 to 026
11. Add 310 # of Blend Y esters to 001
12. Pull sample from 026 & measure soap and sucrose levels, adjust as needed for **run 1C**
13. Add 420 # of Blend Y esters to 026
14. Pull sample from 001 & measure sucrose levels, adjust as needed for **run 1B**
15. Feed **run 1B** from 001, and **run 1C** from 026

Batch 2:

1. Make a normal batch in 001 following Semi-Works procedures (use fresh MeOH no mill chaser), cool with 2450#esters
2. Add 800 lb sucrose and recirculate thru mill and back into 001 for 5hrs
3. Transfer to 026 at the end of first week
4. Feed from 026 for **runs 2A and 2B**

Batch 3:

1. Make a normal batch in 001 following Semi-Works procedures (use fresh MeOH no mill chaser), cool with 2450#esters
2. Add 800 lb sucrose and recirculate thru mill and back into 001 for 5hrs
3. Feed from 001 for **runs 3A, 3B, and 3C**

Prior to starting up R600, pull a vacuum on sucrose feed (and subsequent feed batches before use) and second stage esters for 10 min. **Pull a 4 oz sample of each feed prior to each change in run conditions.** Moistures should be run on sucrose and second stage ester feed every 8 hours and before a new feed batch is brought on stream.Maintain 008, 001, 026, and the catalyst slurry tank 3243 under

N2 throughout the course of the run. The amount of material, following methanol evaporation, is:

Component	Wt per Batch
Sucrose	800
KOH	100
I-1 (soap)	550
Ester	3700
	5150
Methanol requirements	1100

Two catalyst batches are necessary, prepared in 3243, as out-lined in the Semi-Works procedures. The batches should be prepared at the start of each week. The amount of material is:

Component	Wt per Batch
powdered K2CO3	288
Ester	864
	1152

The following is a breakdown of ester requirements for the entire run:

Component	Wt
Stg I	11,100
Stg II	14,600
Catalyst	1728

S. D. Pearson

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G. P. Hawkins
N. J. Holzschuh
J. K. Howie
R. Sarama
J. C. Stewart
S. VanDiest
V. Wee
G. R. Wyness
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INDUSTRIAL CHEMICALS PRODUCT DEVELOPMENT BIWEEKLY REPORT

S. D. PEARSON

PERIOD ENDING JUNE 14, 1989

FG REACTION TECHNOLOGY

Reduced soap feed levels of 50%, 25%, and 0% of normal have been successfully run to high conversions in the 70#/hr pilot plant.

Potassium soap, in concert with the lower sucrose esters produced early in the FG reaction, serves to solubilize the essentially insoluble sucrose/potassium carbonate/methyl ester system. Batch reactions have shown that in the absence of lower sucrose esters soap is required for the reaction to start and proceed. The lower sucrose esters alone, however, are effective sucrose solubilizing agents and since a small amount of soap is generated during the reaction it has been speculated for some time that the continuous system could take advantage of this and significantly reduce or eliminate soap from the feed, given the appropriate operating conditions in the first reactors.

During the first week of the current round of experiments on the 70#/hr system we examined the effects of reduced soap levels in the FG reaction. Feed soap levels of 50%, 25%, and 0% of normal were tested. The sucrose was finely milled and the stage II temperature was lowered to 265°F. At soap levels of 50% and 25% the sucrose utilization was excellent in stage I and the final conversion reached over 95% octaester. We were also very successful with the no-soap process, reacting to 84% octaester, even though sucrose utilization was relatively poor with 1.5% going forward. Visually the crude color appeared excellent; Randy Howard is in the process of working up samples for colors. No burnt sucrose was observed in the crude nor were any mechanical problems experienced due to the low soap levels.

The most interesting results, however, are not in the relative differences in sucrose utilization or final octaester levels, but rather the strong effect soap has on the reaction rate. As soap levels were reduced the rate of esterification increased dramatically in both stage I and stage II; i.e., the no-soap process was faster than the 50% soap process. It is unclear whether these differences are due to viscosity effects or perhaps result from the levels of soap soluble sucrose. This week we plan on following up on the no-soap reaction by changing stage 1 conditions to improve sucrose utilization.

S. D. Pearson

SDP/elg/2041

Keywords: continuous reaction, soap

(19)

RESTRICTED CIRCULATION

RETENTION LIMIT: ORIGINATOR AND LIBRARY - 1/1/94
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CHEMICALS PRODUCT DEVELOPMENT BIWEEKLY REPORT

S. D. PEARSON

PERIOD ENDING JUNE 28, 1989

Low temperature conditions and higher feed rates have been demonstrated on the 70 lb pilot plant.

FG REACTION TECHNOLOGY

Another round of very successful experiments have been completed on the 70 lb/hr pilot plant. The Manufacturing technicians did an great job executing the rather complicated run plan required for P90605, as did the analytical support from SWTC.

As I mentioned in my last biweekly, the first week of experiments centered on soap levels in the feed and demonstrated high conversions could be achieved even at reduced soap concentrations. Colors on samples from these conditions worked up by Randy Howard and Bob Sarama also show a significant improvement as soap level is reduced. While I have no doubts that a very low soap level process is viable, I am much less certain about a no-soap process. In my mind the no-soap process is inherently unstable to process upsets and may, in fact, have multiple steady-states depending upon start-up conditions. The no-soap process clearly needs more work.

During the second week of 70 lb experimentation we examined very low temperatures in stage II & III and also performed a high feed rate run to test the system capability. The low temperature run was at 250°F (25°F below normal) with 2.0 mm Hg in stage II & III and 50% of the normal soap. The conversion reached 95% octaester. Colors are in the process of being worked up. Unfortunately, we observed no improvement in DFK levels at the reduced temperature as batch experiments suggested might be the case. The high feed rate run was 1.5 times the normal and also reach 90%+ octaester content. I believe the 70 lb system will be capable of operating at this increased rate for extended periods of time once the slurry feed pump is replaced (the pump deteriorated much quicker than normal during the run) with a more durable pump.

S. D. Pearson

SDP/elg/2097

Keywords: continuous reaction, soap, temperature

(20)

INTERDEPARTMENTAL CORRESPONDENCE

From: Gene P. Hawkins/S. D. Pearson

Date: September 25,1989

To: Distribution

Retention Limit: 09/1/90

Subject: P90925 Experimental Test Plan

This memo summarizes the run plan for the upcoming 70# run scheduled for the weeks of September 25 and October 2.

OBJECTIVE

The objectives for this run are twofold: to examine the effects of reduced stage III temperature on DFK levels, and to monitor color in product made on the continuous system and refined under conditions that are anticipated for Test Market. A blend of Y esters (86.8%) and hardstock (13.2%) will be used for both weeks of this run.

EXPERIMENTAL

During the week of 9/25 we will examine two reactor conditions. In the first, the system will be brought up on conditions we've run before and plan on using for the extended run during week 2 to confirm that the 70# system is operating properly and to provide an early indication of the color that can be expected. In the second run, for DFK evaluation, the temperature in stage III will be reduced to 230°F and the pressure adjusted to attain approximately 90% octaester out of the last reactor.

The second week will consist of an extended run of roughly 64hrs at 1.5x the normal feed rate. We will be primarily interested in the stability of the system during the reaction phase and will finish up the product using the clinical refining operations. The tubing pump will need to be changed prior to the start of the extended run and once about midway through the run. Once we have reached steady-state, crude should be directed to 3604. Care should be taken so that the temperature of 3604 is kept below 130°F.

A recycle milled sucrose batch will be required for each week. Soap level for both of the catalyst variations will be approximately 33% of normal. Stage I pressure for the entire run will be 15 mm Hg; stage II & III pressure will be 2.0 mm Hg. The reactors are to be emptied at the end of the first week, with no material held for startup the following week.

All the reactors through 607 will be used both weeks. The catalyst injection system will be used to add the carbonate as detailed on the Reactor Conditions Checklist. Two reactors (R600 & R601) are planned for Stage I. Stage II ester addition will be evenly split between R601 & R602. The complete list of experimental conditions for each reactor are shown in the Experimental Conditions Checklist.

1. It is critical that the experimental conditions be closely monitored and adhered to; clear all significant deviations from the run plan through PDD first.

2. Detailed analysis schedules will be posted in the lab. SAMPLES MUST BE TAKEN FROM

EVERY ESTER BLEND. RECORD ADDITIONS TO THE SMALL CATALYST TANK IN THE LOGBOOK.

3. Analytical data are to be control charted as generated; one person will be responsible for this on each shift.

PROPOSED TIMETABLE

Cumulative Time (hr)	Event
0	R600 start-up; close flush mounted ball valve on bottom of R600 then manually fill with slurry feed until level reaches top of agitator; turn agitator on and ensure feed is well mixed before opening flush valve and immediately starting up R600 pump; use two charges from injector initially; once through foaming, fill at reduced rate until level reaches 3" (full vacuum and 275°F)being sure that catalyst injection is on as reactor is filled, then fill at full rate; once level reaches 8in adjust R600 conditions as shown on Checklist
8	R600 through foaming and full, Run 1 feed to drum
9	Feed to R601 and add 1/2 of 2nd stage esters while filling
11	R601 full, feed to drum
12	Feed to R602 and start adding remaining 1/2 of 2nd stage esters to 602 while filling
14	R602 full, feed to R603 and continue to fill to R607
22	All reactors full and feeding forward
37	Run 1 complete, start Run 2 feeding from 001.
61	Run 2 complete. Perform shutdown procedures.

1/28 1:00 THURSDAY 12:30 FRIDAY

use this procedure for start up 2nd week.

** WEEKEND SHUTDOWN

9:15pm, 10/2/89

0	R600 start-up; ~~manually add enough ester heel to allow recirculation through R600 system, once recirculation is established feed from 026 at 55 lb/hr for 20 min to get heel, use two charges from injector initially~~, once through foaming fill at reduced rate until level reaches 3", then fill at 1.5X full rate, being sure that catalyst injection is on as reactor is filled.
8	R600 through foaming and full, Run 1 feed to drum
9	Feed to R601 and add 1/2 of 2nd stage esters while filling @ 1.5X normal rate
11	R601 full, feed to drum
12	Feed to R602 and start adding remaining 1/2 of 2nd stage esters to 602 while filling @ 1.5X normal rate
13	R602 full, feed to R603 and continue to fill to R607
19	All reactors full and feeding forward; continue run
30	change tubing pump.
74	Run 1 complete. Shut down for weekend, dump &rinse reactors, change tubing pump

MATERIALS

All feed vessels should be drop tested prior to use. One sucrose feed batch is needed each week; the soap batches will be be prepared in 001 using a modified clinical procedure:

1) Make soap in 001
2) Add 1000# of blended esters to 001
3) Recirculate thru plate heat exchanger to remove MeOH, set heat exchanger discharge temperature to 220°F and jacket temperature to 150°F
4) Add remaining stage I ester blend (1800# for the first week and 2700# the second) to 001 to cool mixture when MeOH < 1%

Sucrose Slurry Feed Batch:

1) Add 600 lb sucrose in the first slurry batch and 800# in the second before recirculating thru mill and back into 001 (recycle for 3:45 for batch 1 and 5:00 for batch 2).
2) Pull sample from 001 and measure soap and sucrose levels.
3) Feed R600 from 001.

Prior to starting up R600, pull a vacuum on A) sucrose feed batches before use, and B)second stage esters for 20 min. **Pull a 4 oz sample of each feed prior to each change in run conditions.** Moistures should be run on sucrose and second stage ester feed every 8 hours and before a new feed batch is brought on stream. Pull and freeze a 4 oz. sample of each ester blend. Maintain 001, 008, catalyst feed tank, and the catalyst slurry tank (3243) under N2 throughout the course of the run. The amount of material, following methanol evaporation, is:

Component	First Batch	Second Batch
Sucrose	600	800
KOH	27	100
I-1 (soap)	150	550
Blended Ester	2800	3700
	3577	5150
Methanol requirements	600	1100

Two catalyst batches are necessary, prepared in 3243, as outlined in the Semi-Works procedures. The batches should be prepared at the start of each week. The amount of material is:

Component	Wt per Batch

Powdered K2CO3	300
Blended Ester	900
	1200

The following is a breakdown of ester requirements for the entire run:

Component	Wt
Stg I - Blend Y	5,640
I-1	860
Stg II- Blend Y	8,250
I-1	1,250
Catalyst - Blend Y	1,560
I-1	240
Total	17,560

Gene P. Hawkins/S. D. Pearson

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(21)

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RETENTION LIMIT: 10/1/95

CHEMICALS PRODUCT DEVELOPMENT DIVISION-FOOD INGREDIENTS MONTHLY REPORT

S. D. PEARSON

FOR PERIOD ENDING 10/1/89

Three of the key areas of continuous reactor processing that are important for us to understand, no matter what type of olestra we ultimately produce are: Lower operating temperatures, higher reactor pressures, and sucrose utilization. We are making good progress in all areas.

FG REACTION TECHNOLOGY

Over the past several months we've demonstrated that lowering the temperature in Stages II and III results in significantly better product color. By simultaneously reducing soap levels, which increases reaction rates, high octaester conversions can be maintained at temperatures as low as 250°F. During the most recent pilot plant run (P90925) we have extended the range down to 220°F in Stage III while producing 87% octaester product. While the final product color has yet to be worked up, I am anticipating another improvement. Lower processing temperatures also will reduce ester losses during reaction.

The progress made earlier this year around operating pressures clearly demonstrates that high conversions can be made at pressures greater than 5 mm Hg. I am convinced that much higher pressures are possible when we learn how to more efficiently strip MeOH from the crude. Experiments performed by Nelson Holzschuh have quantified sparge effects in a lab batch system, and a series of experiments to investigate alternative sparging techniques such as spraying into the headspace is underway by Steve Alexander and Junan Kao. I am also preparing to run the reaction in a packed column to better understand MeOH removal limitations.

From our wet milling experience on the pilot plant system, and the many experiments performed by Ephraim Kelly and Pat Corrigan, we know that the key to good sucrose utilization is a small sucrose particle size. Gene Hawkins has arranged with Fryma to test a new corundum stone mill head on the 70# system that should dramatically reduce the sucrose particle size. Unfortunately, particle size alone isn't enough to ensure good utilization at very low soap levels. Data we have collected over the last year suggests that I-bar, free sucrose, and soap levels are not independently variable, and at low soap levels all the sucrose is not esterified even with small particle sizes.

S. D. Pearson 10/2/89

SDP/elg/2277

S. D. Pearson

Key Words: temperature, pressure, sucrose utilization, filtration

22

INTERDEPARTMENTAL CORRESPONDENCE

From: Gene P. Hawkins/S. D. Pearson — Date: January 22,1990

To: Distribution — Retention Limit: 1/1/91

Subject: P ~~00129~~ Experimental Test Plan
00205

This summarizes the run plan for the 70# run scheduled for the weeks of 1/29 and 2/5/90.

OBJECTIVE

The objectives for this run are to examine the effects of a) sucrose milled using the Fryma corundum stone head, b) carbon dioxide sparging, c) high system pressures (25mm Hg) on all the reactors, and d) variation of ester addition levels. A blend of Y esters (87.8%) and hardstock (~~13.2%~~) will be used for both weeks of this run.

13 ~~15~~ 87 ~~85~~

EXPERIMENTAL

During the week of 1/29, we will examine two milling treatments of sucrose, utilizing different gap settings with the new corundum stone head recently purchased from Fryma. Following this will be a run using carbon dioxide as a sparging gas in R603-5. The final run of the week will use 25mm Hg pressure across the reaction train, with the aim of producing material of 75% Octa from the last reactor.

The second week will consist of runs at varying ester levels and temperatures. The current mole ratio is about 14:1 ester:sucrose. The three ratios to be investigated will be 12:1, 8.5:1, and 10:1, in that order. The final two runs planned will see the ester ratio restored to 14:1, and Stage I temperatures of 265F and 255F.

As outlined above,one sucrose batch will be required for the first week's operation. One full slurry batch will be required for the second week, with the possible need for a small supplementary batch. Soap level for both weeks will be approximately ~~50%~~ 62.5% of normal. Stage I pressure for the first two runs of the week of 1/29 will be 15 mm Hg; stage II & III pressure will be ~~30~~ 25 mm Hg. Pressures for the final run of that week will be 25mm Hg across all reactors. The reactors are to be emptied at the end of the first week, with no material held for startup the following week.

All the reactors through 607 will be used both weeks. The catalyst injection system will be used to add the carbonate as detailed on the Reactor Conditions Checklist. Two reactors (R600 & R601) are planned for Stage I. Stage II ester addition will be evenly split between R601 and R602 during the week of ~~1/29~~ 125 ppm, and as directed by PDD during the week of ~~2/5~~. 312 ppm The complete list of experimental conditions for each reactor are shown in the Experimental Conditions Checklist.

1. It is critical that the experimental conditions be closely monitored and adhered to; clear all significant deviations from the run plan through PDD before implementing.

2. Detailed analysis schedules will be posted in the lab. SAMPLES MUST BE TAKEN FROM EVERY ESTER BLEND. RECORD ADDITIONS TO THE SMALL CATALYST TANK IN THE LOGBOOK.

3. Analytical data are to be control charted as generated; one person will be responsible for this on each shift.

PROPOSED TIMETABLE

Cumulative Time (hr)	Event
0	R600 start-up: close flush mounted ball valve on bottom of R600 then manually fill with slurry feed until level reaches top of agitator; turn agitator on and ensure feed is well mixed before opening flush valve and immediately starting up R600 pump; use two charges from injector initially; once through foaming, fill at reduced rate until level reaches 3" (full vacuum and 275°F)being sure that catalyst injection is on as reactor is filled, then fill at full rate; once level reaches 8 in adjust R600 conditions as shown on Checklist
8	R600 through foaming and full, **Run 1(MIII Setting I)** feed to drum
9	Feed to R601 and add 1/2 of 2nd stage esters while filling
11	R601 full, feed to drum
12	Feed to R602 and start adding remaining 1/2 of 2nd stage esters to 602 while filling
14	R602 full, feed to R603 and continue to fill to R607
22	All reactors full and feeding forward
37	**Run 1 complete. Start Run 2 (MIII Setting II)** feed from ___.
49	**Run 2 complete. Start Run 3(CO2 Sparge);** feed from 026.
61	**Run 3 complete. Start Run 4 (25mm Hg);**feed from 026.
85	Run 4 complete. Empty all reactors for weekend shutdown.

* * WEEKEND SHUTDOWN

0	R600 start-up;close flush mounted ball valve on bottom of R600 then manually fill with slurry feed until level reaches top of agitator; turn agitator on and ensure feed is well mixed before opening flush valve and immediately starting up R600 pump; use two charges from injector initially; once through foaming, fill at reduced rate until level reaches 3" (full vacuum and 275°F)being sure that catalyst injection is on as reactor is filled, then fill at full rate; once level reaches 8 in adjust R600 conditions as shown on Checklist
8	R600 through foaming and full, **Run 1 (12:1)** feed to drum
9	Feed to R601 and add 2nd stage esters as directed by PDD.
11	R601 full, feed to drum
12	Feed to R602 and add remaining 2nd stage esters to 602
13	R602 full, feed to R603 and continue to fill to R607
19	All reactors full and feeding forward; continue run
34	**Run 1 complete. Start Run 2 (8.5:1).**
58	**Run 2 complete. Start Run 3 (10:1).**
82	**Run 3 complete. Start Run 4 (14:1,265F Stage I).**
94	**Run 4 complete. Start Run 5 (14:1,255F Stage I).**
106	Run 5 complete. Empty and rinse reactors, change tubing pump.

MATERIALS

All feed vessels should be drop tested prior to use. One full sucrose feed batch is needed the first week; one full batch with the possibility of an additional smaller one the second.

The soap batches will be be prepared in 001using a modified clinical procedure:

1) Make soap in 001
2) Add 1000# of blended esters to 001
3) Recirculate thru plate heat exchanger to remove MeOH, set heat exchanger discharge temperature to 220°F and jacket temperature to 150°F
4) ~~Add remaining stage I ester blend to 001 to cool mixture when MeOH < 1%~~

soap: 22

STORE SOAP IN 501 UNDER N_2 UNTIL needed for feed batches. ADD as directed by PDD to get ½ soap levels in feed batches. (SOP)

Sucrose Slurry Feed Batch:

1) **Batch 1**: Add 800 lb sucrose to the slurry batch; mill approximately ~~one-fourth~~ ⅓ of the batch using the corundum stone head (single pass) and pump to 026. This is the feed for **Run 1.** At the end of this run, reset the mill head gap as directed, and ~~mill another one fourth for Run 2~~. RECYCLE Mill BACK INTO 001
2) Pull sample from 026 & 001 and measure soap and sucrose levels.
3) Feed R600 from 026 for Run 1
4) Set the mill gap as directed by PDD for all subsequent variations.

Prior to starting up R600, pull a vacuum on A) sucrose feed batches before use, and B)second stage esters for 20 min. **Pull a 4 oz sample of each feed prior to each change in run conditions.** Moistures should be run on sucrose and second stage ester feed every 8 hours and before a new feed batch is brought on stream. Pull and freeze a 4 oz. sample of each ester blend. Maintain 026 and the catalyst slurry tank (3243) under N2 throughout the course of the run. The amount of material, following methanol evaporation, is:

Component	Each Batch
Sucrose	800
KOH	100
I-1 (soap)	550
Blended Ester	3700
	5150
Methanol requirements	1100

Two catalyst batches are necessary, prepared in 3243, as outlined in the Semi-Works procedures. The batches should be prepared at the start of each week. The amount of material is:

Component	Wt per Batch
Powdered K2CO3	300
Blended Ester	900
	1200

The following is a breakdown of ester requirements for the entire run:

Component		Wt
Stg I -	Blend Y	5,640
	I-1	860
Stg II-	Blend Y	8,250
	I-1	1,250
Catalyst -	Blend Y	1,560
	I-1	240
Total		17,560

adjust to 15% I-1 85% Blend Y

Gene P. Hawkins/S. D. Pearson

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1. Clean+dry 001 + 026

001 → I-1 550

1st Blend 008 → I-1 825 + Y 4675 = 5500

RCon 35

3700 Sucrose

900 Catalyst

900

2nd → 900 residual I-1 690 + Y 3910

add 4600 →

Gary Busch + company

Hampshire House: Tri-City 772-5440 x344

- put on old mill head
- dump 026 - 001
- Recycle mill for 3 hrs back into 001
- mill set at ¼ turn off stop
- pump speed at 30-40%
- run samples on feed batch as noted on analytical sheet
- start up conditions are for run 1A

TO 001
- Take 550 # soap & ester from 501
- Take 3370 # Blend from 008
- Add 800 # sucrose

CATAL SLURRY 2.8058
YST

SUCROSE SLURRY
2.9121.

(23)

INTERDEPARTMENTAL CORRESPONDENCE

From: S. D. Pearson

Date: March 19,1990

To: Distribution

Retention Limit: 01/1/91

Subject: **P00326 Experimental Test Plan**

This memo summarizes the run plan for the upcoming 70# run scheduled for the weeks of March 26 and April 2.

OBJECTIVE

The objective for this run is to continue DFK experimentation on the 70# system. Straight 185 esters will be used for both weeks of this run. The hardstock ester for soap making has been redistilled prior to the run in order to reduce its CO and PV.

EXPERIMENTAL

During the week of 3/26 we will examine three reactor conditions. The first two runs will involve ester:sucrose mole ratios of roughly 9:1. This will be obtained by reducing stage II ester flow to R601 to 30#/hr and eliminating ester feed to R602. In addition to the lower ester:sucrose ratio, the second run will use CO2 sparging instead of N2, as in P00205. The final condition for week one will be at 60mmHg in stages II & III. A normal ester:sucrose ratio and N2 sparge will be used for run three (although the sparge rate will be significantly increased). DFK samples will be taken once we reach steady-state and promptly analyzed at SW.

The second week of experiments starts with a control run at 13.5:1 E:S, 3.0 mmHg, 275°F/265°F, and N2 sparge. Following this, our next run will replicate our best condition of the prior week to confirm our DFK result. We will undoubted run this condition out for an extended time to collect crude to further work up through refining. If time permits we may try one additional condition as a follow-up to week one experiments.

Stage II & III pressures should be monitored throughout the entire two week run with the McCloud gage or manometer. Local temperatures will be used for reactor pot control. The corundum mill will be used on a once through basis to mill from 001 to 026; adjusted to a load of 17-18amps at 80% of 001 pump max with back pressure around 50 psig (start-up in recycle mode for 10 min to ensure stability before milling to 026). Catalyst will be made and stored in 501. One soap batch will be made at the start of the first week with 1/3 of it going into each of the three sucrose feed batches (≈ 550#). Excess soap should be kept in a tote under N2 with tempered water heating.

The reactors are to be emptied at the end of the first week, with no material held for startup the following week.

All the reactors through 607 will be used both weeks. The catalyst injection system will be used to add the carbonate as detailed on the Reactor Conditions Checklist. Two reactors (R600 & R601) are planned for Stage I. Stage II ester addition will be evenly split between R601 & R602. The complete list of experimental conditions for each reactor are shown in the Experimental Conditions Checklist.

1. It is critical that the experimental conditions be closely monitored and adhered to; clear all

significant deviations from the run plan through PDD first.

2. Detailed analysis schedules will be posted in the lab. SAMPLES MUST BE TAKEN FROM EVERY ESTER BLEND. RECORD ADDITIONS TO THE SMALL CATALYST TANK IN THE LOGBOOK.

3. Analytical data are to be control charted as generated; one person will be responsible for this on each shift.

PROPOSED TIMETABLE

Cumulative Time (hr)	Event
0	R600 start-up: close flush mounted ball valve on bottom of R600 then manually fill with slurry feed until level reaches top of agitator; turn agitator on and ensure feed is well mixed before opening flush valve and immediately starting up R600 pump; use two charges from injector initially; once through foaming, fill at reduced rate until level reaches 3" (full vacuum and 275°F)being sure that catalyst injection is on as reactor is filled, then fill at full rate; once level reaches 8in adjust R600 conditions as shown on Checklist to **Run 1**, feeding from 026.
8	R600 through foaming and full, **Run 1** feed to drum
9	Feed to R601 and 2nd stage esters while filling
10	R601 full, feed to drum
11	Feed to R602 and continue to fill to R607
25	All reactors full and feeding forward
44	**Run 1** complete, start **Run 2** feeding from 026.
80	**Run 2** complete, change tubing pump, start **Run 3** feeding from 026.
104	**Run 3** complete. Perform shutdown procedures.

** **WEEKEND SHUTDOWN**

0	R600 start-up: close flush-mounted ball valve on bottom of R600 then manually fill with slurry feed until level reaches top of agitator; turn agitator on and ensure feed is well mixed before opening flush valve and immediately starting up R600 pump; use two charges from injector initially; once through foaming, fill at reduced rate until level reaches 3" (full vacuum and 275°F)being sure that catalyst injection is on as reactor is filled, then fill at full rate; once level reaches 8in adjust R600 conditions as shown on Checklist to **Run 4**, feeding from 026.
8	R600 through foaming and full, **Run 1** feed to drum
9	Feed to R601 and 2nd stage esters while filling
10	R601 full, feed to drum
11	Feed to R602 and continue to fill to R607
25	All reactors full and feeding forward
44	**Run 4** complete, start **Run 5** feeding from 026.
95	change tubing pump. shut down as required.

MATERIALS

All feed vessels should be drop tested prior to use. Three sucrose feed batches (at 1/3 soap levels)are needed; one soap batch will be be prepared in 001 using a modified clinical procedure:

1) Make soap in 001
2) Add 1000# of blended esters to 001
3) Recirculate thru plate heat exchanger to remove MeOH, set heat exchanger discharge temperature to 220°F and jacket temperature to 150°F
4) Weigh 550# to clean drum for use in first sucrose feed batch and store remainder in clean tote under N2 with tempered water heating. Weigh 550# from tote for subsequent sucrose batches.

Sucrose Slurry Feed Batch:

1) Add 3370# 185 ester and 800 lb sucrose. Pull sample from 001 and measure soap and sucro levels.
2) Mill as directed by PDD on a once-through basis from 001 to 026. Pull sample from 026 and measure moisture.
3) Feed R600 from 026.

Prior to starting up R600, pull a vacuum on A) sucrose feed batches before use, and B)second stage esters for 20 min. **Pull a 4 oz sample of each feed prior to each change in run conditions.** Moistures should be run on sucrose and second stage ester feed every 8 hours and before a new feed batch is brought on stream. Pull and freeze a 4 oz. sample of each ester blend. Maintain 026 and the catalyst slurry tank (3243) under N2 throughout the course of the run. The amount of material, following methanol evaporation, is:

Component	First Batch	Second Batch	Third Batch
Sucrose	800	800	800
KOH	100	100	100
1-1 (soap + ester)	550	550	550
185 Ester	3350	3350	3350
	4800	4800	4800
Methanol requirements	1100	1100	1100

Two catalyst batches are necessary, prepared in 501, as outlined in the Semi-Works procedures. The batches should be prepared at the start of each week. The amount of material is:

Component	Wt per Batch
Powdered K2003	300
185 Ester	900
	1200

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CH900001

(24)

INTERDEPARTMENTAL CORRESPONDENCE

NCN-CONFIDENTIAL

From: S. D. Pearson

DO NOT DUPLICATE

Date: 7/12/90

To: Distribution

Subject: DFK Experimental Summary

Attached is the DFK report summarizing the reaction work the DFK team has been pursuing the last several months. A thorough review of clinical lots during the past year confirms that even under the current processing conditions we can routinely expect to make less than 300ppm product at a target of 75% octaester for ester feedstocks such as I85 Soy or CS. In addition, we have experimentally identified the effects of several process parameters, ester and catalyst types, sparge gases, as well as filtration and post reaction treatment on DFK formation in lab and pilot plant scale reaction systems, ultimately leading to process conditions that produce uniquely low ketone levels. The combination of 225°F in stage II along with high nitrogen sparge and an ester:sucrose ratio of 9:1 was effective in reducing the ketone level in evaporated Olestra down to 130ppm at 75% octaester. By also reducing DFK brought in with the feed esters a further 10%-25% decrease product ketones may be realized. Further experimental work still needs to be pursued around temperature/sparge/ester ratio to optimize the reaction conditions. The results of these experiments should be translated to the clinical system as soon as possible to further aid in DFK control.

Scott D Pearson

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CH9000001

IX. PILOT PLANT DFK EXPERIMENTS

(S.Pearson)

The continuous pilot plant system was used to conduct a series of fourteen experiments aimed at understanding the effects of various processing variables on DFK formation. Historical data, based on [redacted] esters, indicates that the continuous system produces lower, more consistent levels of DFK than the clinical system and that it is relatively insensitive to modest changes in temperature, pressure, MeOH levels, and reaction rates (see Clinical and Pilot Plant DFK Levels at 75% Octaester). This new set of experiments, performed with I85 esters, extends the range of conditions explored on the pilot plant to include the effects of ester:sucrose ratio, nitrogen sparge rate, high pressure operation in stage II, sparging with carbon dioxide, and low temperature processing.

The learnings from these experiments confirm some of the DFK trends observed on small scale systems regarding, for example, ester:sucrose ratio and temperature, while additionally suggesting that the mass transfer effects that can dominate need to be well understood in order to ensure meaningful scale-up of lab or pilot plant data. By understanding these effects on the pilot plant scale we have been able to identify promising conditions to further reduce DFK formation while overcoming the traditional FG reaction rate trade-offs seen on lab systems.

A. Pilot Plant Experimental

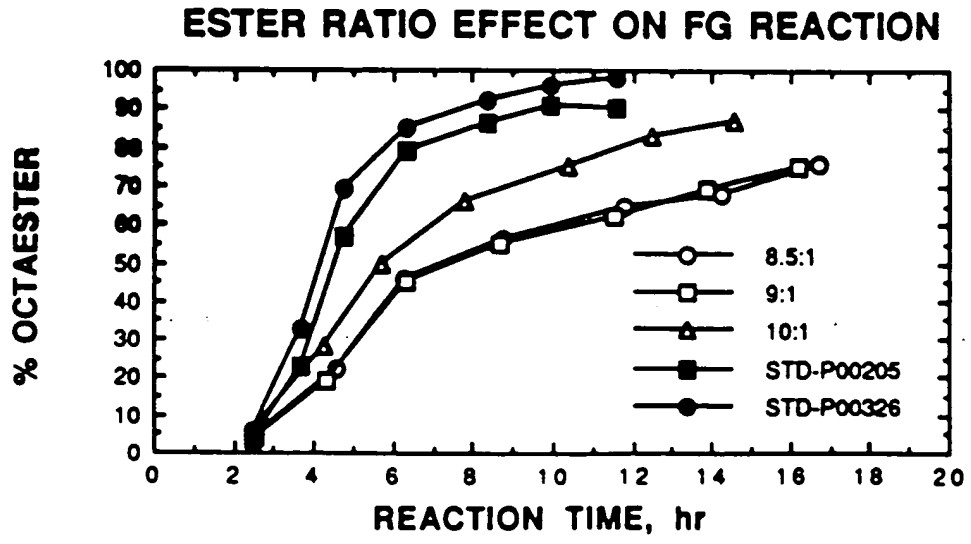
The DFK experiments summarized below are from pilot plant runs P00205 and P00326. Straight I85 esters were used for all runs, as well as powdered carbonate and corundum milled sucrose. Hardstock soap mole ratio to sucrose was 0.26:1 in stage I (1/3 soap), along with a 5:1 ester:sucrose ratio. Catalyst levels were maintained in the 0.2% - 0.6% range for all reactors. Stage I operating conditions were 15mmHg, 275°F, 700rpm, and a total residence time of 2.5hr.

Stage II ester addition was directed to the second reactor in stage I, with any amount in excess of a 9:1 ratio added to the first reactor in stage II. Unless otherwise noted for an individual run, the stage II operating conditions for the various experimental runs were: 265°F, 0.2 lb/hr N2 sparge, 3.0 mmHg, 650rpm, and an ester:sucrose mole ratio of 13.5:1.

B. Results and Discussion

1. Ester:Sucrose Ratio.

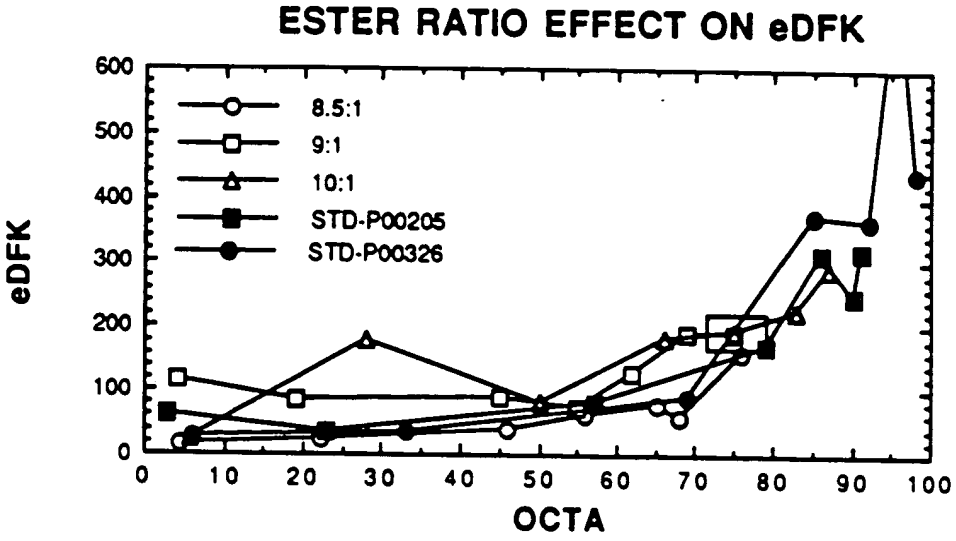
The molar ratio of total methyl ester to feed sucrose was varied from the standard condition of 13.5:1 down to 8.5:1. As the ratio is reduced, the FG reaction slows as shown in the following figure. The esterification rates dropped roughly two to three-fold in going from high to low excess



esters. For example, it took just over 5 hrs of reaction time to reach 75% octaester at a 13.5:1 ester:sucrose level, while the reaction time tripled to nearly 16 hrs at 8.5:1. Reaching the higher octaester levels at the lower mole ratios would be a production problem under standard operating conditions because the reactor volume is relatively fixed, suggesting capacity may have to be traded-off.

The longer residence times of the pilot plant for the lower ester ratios also caused the methanol levels in each reactor to be reduced by about 35%, since the stripping capacity of the system was constant for the five runs. MeOH concentrations ranged from 50ppm to 15ppm over the last four reactors at 13.5:1.

While there is a noticeable effect on the FG reaction, the influence on the DFK reaction is less clear. In the figure below are plotted the estimated DFK (eDFK) values for finished product, obtained by multiplying crude DFK measurements by an appropriate correction factor based on a material balance in each reactor,versus octaester level in each of the last seven reactors. The box



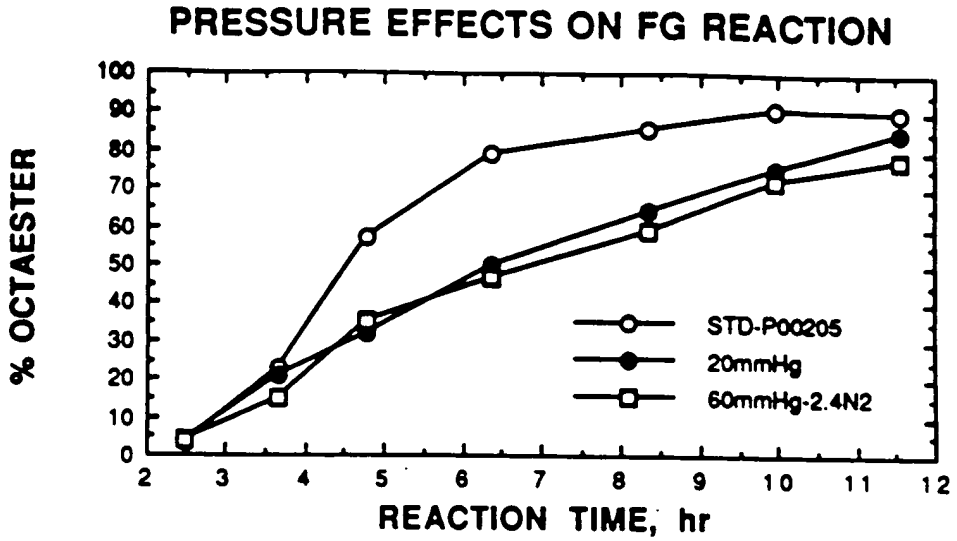
located at 75% octa and 186ppm eDFK represents the operating window as defined from the historical data on IMF esters; the dimensions of the box are two standard deviations from the mean values.

All the eDFK values pass through the historical box, independent of ester ratio. There was also no net lowering of DFK attributable to the I85 esters alone, unlike the clinical system which showed a 32% reduction. Additionally, neither the increase in reaction times from 5hr to 16 hr, nor the differences in MeOH levels mentioned above appeared to influence DFK concentrations. This is certainly surprising since lab data and kinetic simulation suggested each of these should cause a change in ketones. It seems that the pilot plant system, under these standard conditions, is operating in a much different mass transfer regime than either of these models and is effectively moderating large perturbations of some of the DFK reaction parameters.

2. High Stage II Pressure.

Three stage II operating pressures were run: 3.0mmHg, 20.0mmHg, and 60.0mmHg. Sparge rates were increased to 0.8lb/hr and 2.4lb/hr to compensate for the reduced gas velocity at the higher pressures in order to reach the desired octa conversion (while the velocities at 20.0mmHg and 60.0mmHg were roughly equivalent, the velocity at 3.0mmHg with 0.2lb/hr N2 was actually 67% higher).

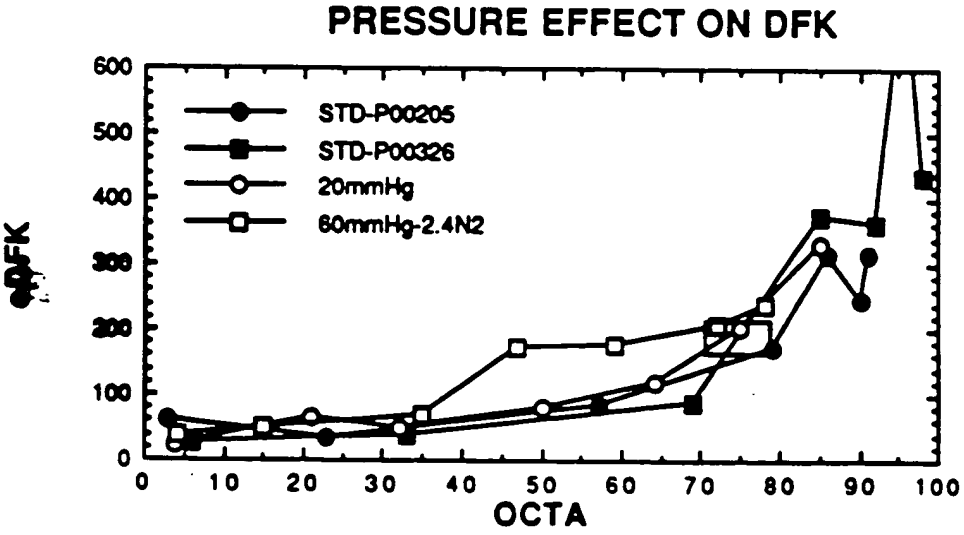
In the figure below, the percent octaester is plotted for each run. Good FG reaction rates can be



seen at all pressures thru 60mmHg, and would clearly be possible at higher pressures with the appropriate adjustment in sparge. The relatively faster rate at 3.0mmHg is due to the higher gas velocities as noted above.

MeOH levels were not substantially different between the three runs, ranging from 100ppm thru 20ppm in the last 5 reactors.

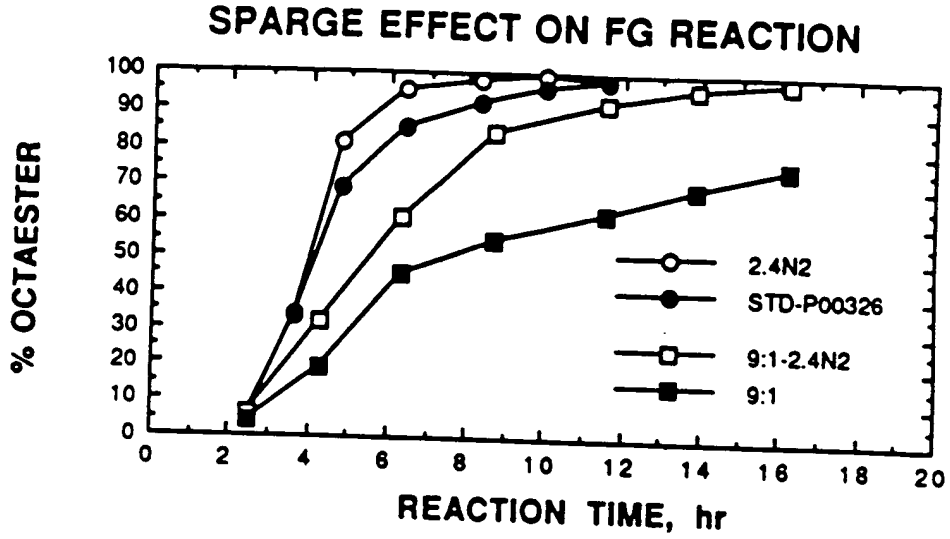
The resulting DFK concentrations for each pressure at the various octaester levels is shown below. Again, the box represents the historical data at 75% octa, which all trajectories pass thru.



From this data it seems clear that pressure alone does not affect DFK formation, stripping conditions as a whole probably need to be considered.

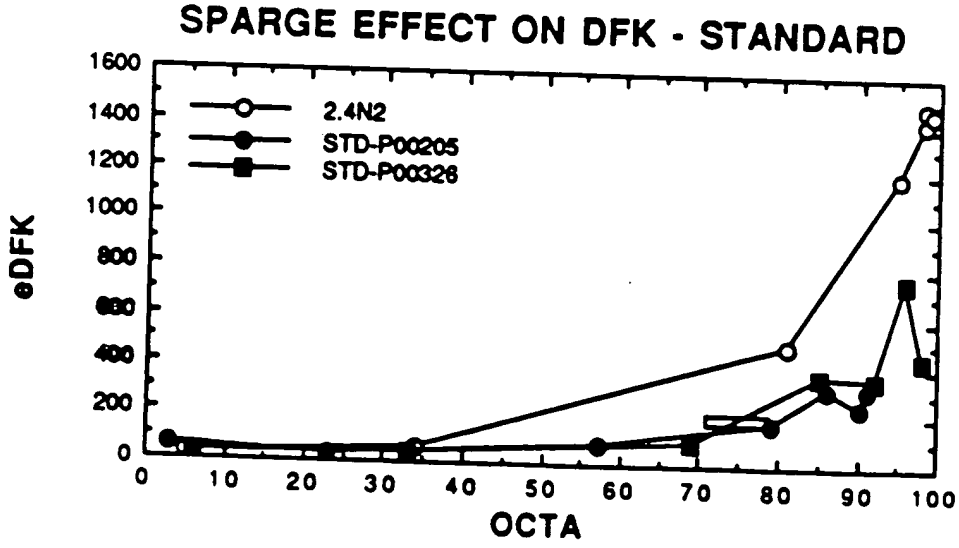
3. Nitrogen Sparge.

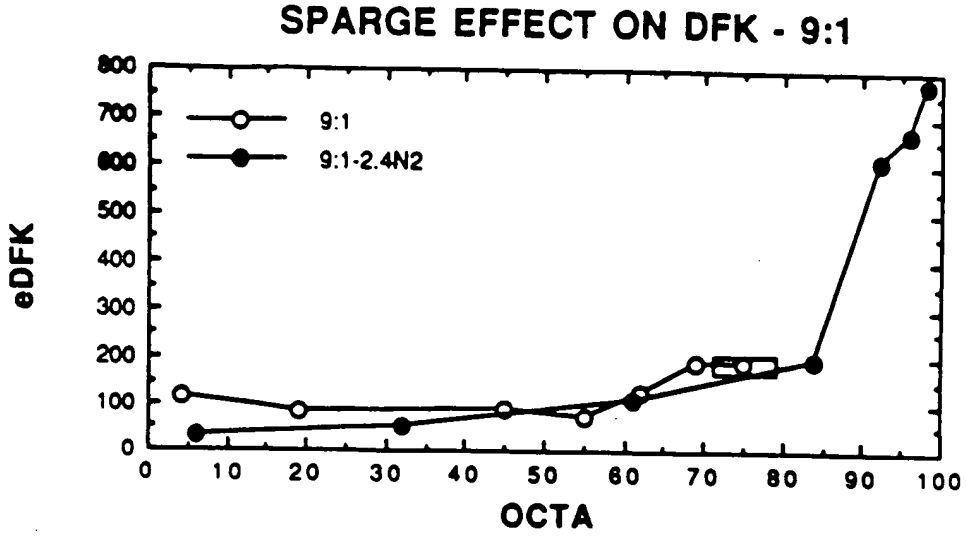
Two levels of nitrogen sparge were tested, 0.2lb/hr and 2.4lb/hr. The enhancement in the FG reaction rate is readily seen in the following figure at ester:sucrose levels of 13.5:1 and 9:1. For



the high ester ratio the FG reaction rate increased by about a factor of three in going to higher sparge rates, while at 9:1 the reaction rate increased by roughly a factor of four. Both agree reasonably well with the expected increase in mass transfer coefficient, k_La_B, for a twelve-fold sparge velocity increase.

The DFK levels are graphed below for the high nitrogen sparge experiments. The first figure compares the standard 0.2lb/hr sparge rate with high sparge at 13.5:1 ester:sucrose ratio and the





second figure illustrates the effect at 9:1. At high stripping conditions there is a markedly different response of the system depending on the ester:sucrose ratio; the 13.5:1 ratio shows just over a doubling in DFK values while at 9:1 there in no discernable effect.

It seems likely that this result is due to the ester ratio effect that has been noted in lab reactions, but was not apparent in the earlier experiments performed on the continuous system because of mass transfer limitations. The high sparge rates reduce mass transfer limitations enough so that mass-action terms such as ester:sucrose ratio become important. The reduction in MeOH concentrations was probably not a contributing factor, since the longer residence times and slower MeOH evolution rates at 9:1 gave lower MeOH levels, particularly at high sparge conditions, yet the 9:1 did not produce higher ketones.

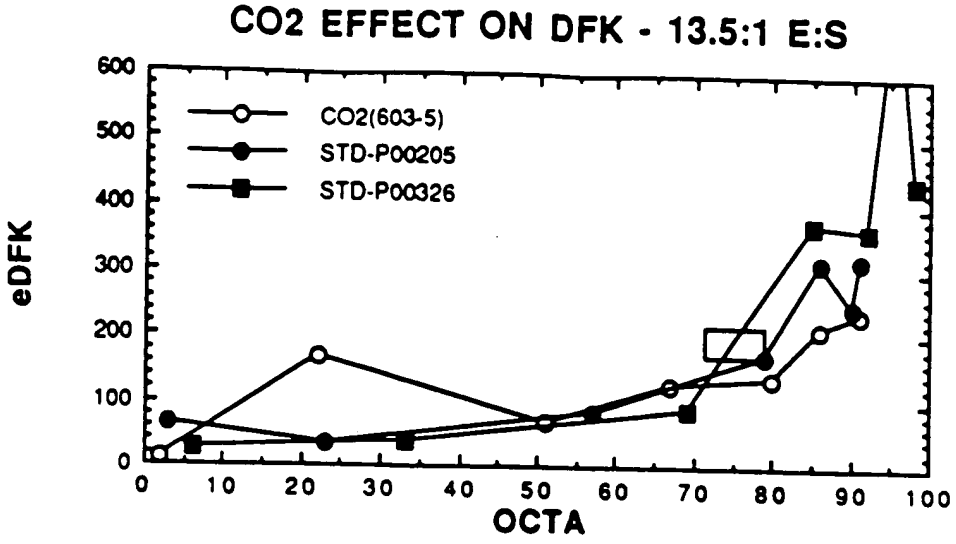
The lack of an increase in DFK at 9:1/high sparge rates, coupled with the quadrupling of the FG reaction rate, allows us to break the trade-off in manufacturing capacity that lab scale experiments suggested were required to control at low DFK levels.

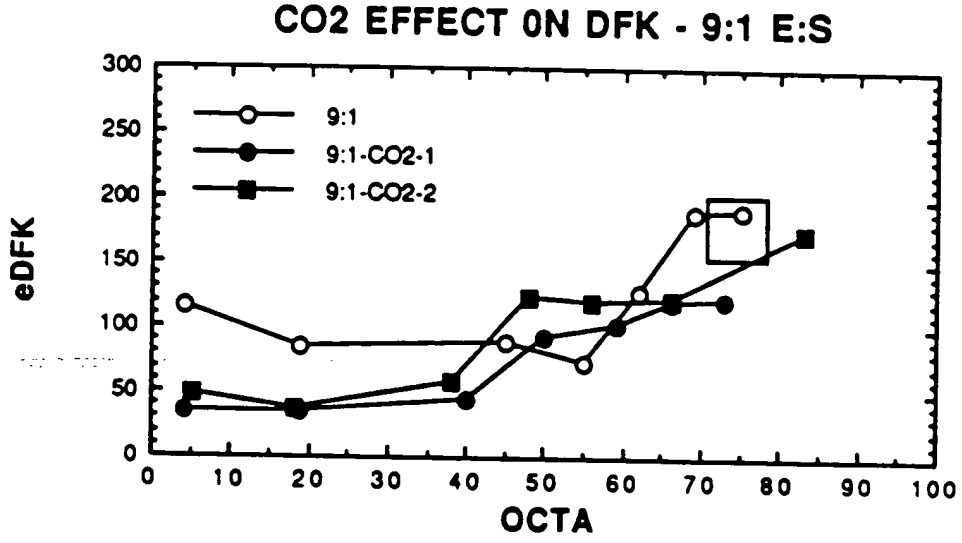
4. Carbon Dioxide Sparge.

Four CO_2 sparging experiments were performed, one at 13.5:1 ester:sucrose and the others at 9:1. Sparge rates were set at the standard 0.2 lb/hr for all except the last run which was set at 2.4lb/hr. CO_2 was run from ultra high purity grade cylinders.

FG reaction rates and conversions were comparable whether CO_2 or N_2 was the sparge gas, with the exception of the high sparge rate experiment where relatively low octaester levels were reached ([redacted]), probably due to the impurities in the slightly lower grade CO_2 used for this run.

DFK results for the runs are shown in the following two figures, the first at 13.5:1 and the second at an ester ratio of 9:1. The DFK level is lower than the historical data at the standard e:s ratio, where only the reactors at 50%, 65% and 80% were CO_2 sparge, the rest were N_2 sparged. At the lower e:s ratio, where all reactors were CO_2 sparged, the ketone level is also reduced on average. In fact, the DFK concentrations average about 25% lower for both ester ratios





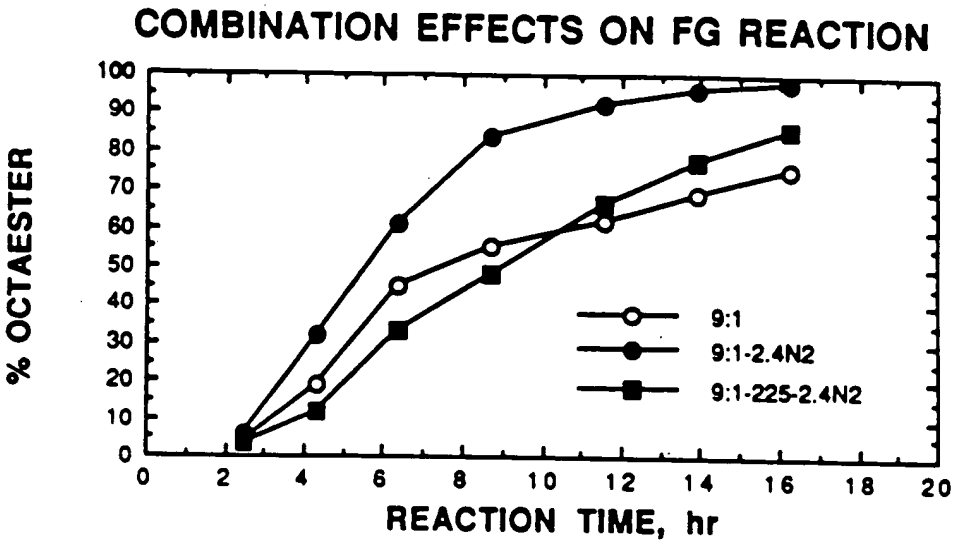
(~ 145ppm), which is reasonable since the two should have nearly equivalent liquid phase CO_2 concentrations that would in turn effect the DFK reaction in a similar way .

While CO_2 sparging does appear to yield lower DFK levels than N_2 sparging, more work needs to done regarding minimum gas purity requirements, not only as it effects the FG reaction, but also in regards to product color and odor.

5. Temperature

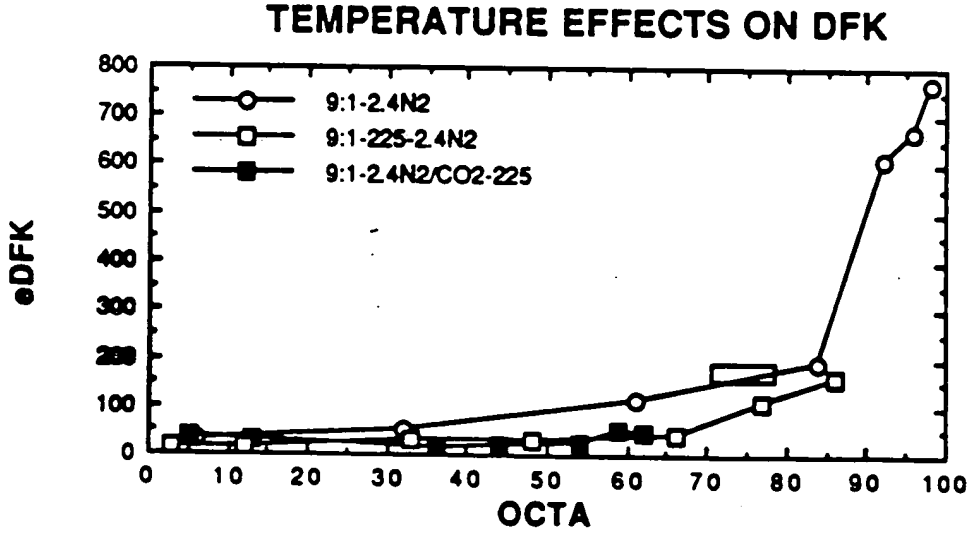
Previous pilot plant runs have investigated the effects of lower reaction temperatures in stage II of the esterification reaction. Low temperatures significantly slow the reaction and reduce the amount of color bodies formed. At temperatures down to 250°F there was no observable DFK reduction, at 225°F DFK determination was not possible due to a contamination of the crude with trace quantities of seal oil.

In this experiment, DFK levels at 225°F and 265°F are compared. A high nitrogen sparge rate and 9:1 ester ratio was used, based on the learnings discussed above. Plotted below are the octaester levels as a function of reaction time for three runs: 9:1 at low sparge and 265°F, 9:1 at



high sparge and 265°F, and 9:1 at high sparge and 225°F. The reaction rate increases as the sparge is increased then decreases as the temperature is dropped to 225°F. The apparent activation energy calculated from the above data is 20.6kcal/mol, which agrees well with previous calculations. The rate at 225°F is quite adequate for production purposes.

The associated DFK values are shown below for the two high N_2 sparge runs, plus an additional run with both high N_2 and CO_2 sparging. The DFK levels are well below the historical data, and



in fact, in the 130ppm range when the temperature is at 225°F. The data from the combined N_2/CO_2 run is included, even though high octaester was not reached due to CO_2 contamination, to illustrate that the reduced temperature trend is consistent.

These levels of DFK are well below what has been demonstrated by other techniques that relied on simply slowing down the esterification reaction. In all those cases the slowdown was to such an

extent that production capacity would have been profoundly reduced. Here we have broken the esterification rate trade-off while simultaneously producing uniquely low levels of DFK.

C. Conclusions & Recommendations

DFK experiments were performed on the continuous pilot plant to explore the effects of excess esters, sparge rates and gases, high pressures, and low temperature operation. The learnings from these runs include:

1) The amount of excess esters present may influence the DFK levels in product if the reaction operating conditions are appropriately adjusted. Under standard conditions there is no discernable ester effect, but when operating in a significantly reduced mass transfer regime the DFK levels can differ by a factor of two or more at 75% octaester. There was no reduction below the historical 186±45ppm level that could be attributed to ester ratios, down to 8.5:1.

   This observation suggests that lab batch results which show large excess ester effects are probably not scaleable because the experiments were conducted under much different, and uncharacterized mass transfer limitations.

2) The operating pressure in stage II had no effect on DFK levels. This is undoubtedly due in this experiment to the relatively constant stripping conditions that were maintained. The stripping conditions are restrained on the continuous system because of the finite reactor residence times that can be achieved while still maintainng at least 75% octaester product. Again, lab batch results from uncharacterized systems which indicate pressure effects are difficult to realize on larger systems.

3) High levels of nitrogen sparge increased DFK levels at high ester ratios, but had no noticable effect on ketones at an ester ratio of 9:1, thru conversions of 80% octaester. This effect is probably a result of mass transfer limitations reduced to the point where ester mass-action then becomes a dominant term. MeOH concentrations are unlikely to be the reason since the longer residence times and slower MeOH evolution rates at 9:1 gave lower liquid phase MeOH values, but also yielded lower DFK.

   The fast esterification rates at high sparge condition along with low excess esters allows us to greatly simplify the FG making process by reducing or eliminating ester recycle, etc., without increasing ketones above the historical base or compromizing manufacturing capacity.

4) Using CO_2 as the sparging gas was effective in reducing DFK by roughly 25% compared to historical data at 75% octaester. Presumably, higher liquid phase concentrations achieved by raising the pressure would be more effective. The purity of CO_2 required, however, needs to be defined because one source of ultra high purity CO_2 may have caused the FG reaction to stop ~ 60%.

5) Low temperature processing yielded the lowest level of DFK. In combination with a 9:1 ester ratio and high nitrogen sparge, a stage II temperature of 225°F yielded ketones in the 130ppm range at 75% octaester. Again, this selectivity effect would probably not be observable if we weren't also operating in a regime of greatly reduced mass transfer resistances.

   This set of conditions breaks the esterification rate trade-off that other processing options require to control DFK while simultaneously producing uniquely low levels of ketones.

6) In comparing similar reaction conditions, the pilot plant showed no observable change in DFK that could be traced to ester type, unlike the clinical system where IMF esters react faster and give much higher ketone levels. The differences in mass transfer between the two systems may be responsible for this behavior.

   Moving the clinical system toward the low temperature, low excess ester and high sparge rates learnings from these experiments should further reduce ketone formation during normal production.

These experiments have refined our thinking and shown us new opportunities for methods to control and reduce DFK in product. The importance of characterizing mass transfer limitations is of paramount importance as we attempt to transfer learnings from lab to pilot scale, and will continue as we move up to test market production.

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(25)

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INDUSTRIAL CHEMICALS PRODUCT DEVELOPMENT BIWEEKLY REPORT

S. D. PEARSON

PERIOD ENDING APRIL 19, 1989

Recent pilot plant and lab data indicates that sucrose utilization in stage I can influence the final conversion.

The purpose of the most recent 70#/hr pilot plant run P90327 was to evaluate various location options for the sucrose feed mill in the Test Market system. Three experiments were run under standard reaction conditions (15.0 mmHg in stage I and 2.0 mmHg in stages II & III) but differed in the way the sucrose feed batch was milled. Two batches were milled in a once-through mode, one was 16% sucrose with soap while the other was 30% sucrose without soap, a third batch of 16% sucrose with soap was milled in a recycle mode for approximately 2.5 turnovers. I expect that the three milling methods gave different particle sizes, in a decreasing fashion as listed above. Dave Maltbie and Bill Hughes are currently doing particle size analysis to verify this. The same esters were used for all three batches.

All three experiments ran well and excellent steady-state data was obtained. The way in which the sucrose was milled had a big impact on stage I sucrose levels. The batch that was recycle milled had less than 0.2% sucrose in the effluent of R601 while the once-through, 16% sucrose with soap, had exit levels of 0.5-0.7%. The larger the particle size the less effectively sucrose was utilized.

The most startling observation was not in stage I, however, but in stage III. The final conversions varied from 89% to 95%, with the highest conversions coming from the recycle milled batch! It seems clear that unless sucrose is effectively used early in the reaction it will continue to enter late resulting in lower final octaester conversions in the continuous system.

On a recent lab batch experiment Nelson Holzschuh filtered the crude to remove unreacted sucrose when the sucrose level dropped to 1-2% then recatalyzed and continued. The reaction reached 95% octa in 2 hours while an unfiltered control run reached 88% octa in four hours. The reaction rate in stage II & III seems to depend on how much residual sucrose remains from stage I.

The next series of experiments on the 70#/hr pilot plant will be aimed at understanding the effects of particle size on conversion. In practice, we may simply want to filter the sucrose feed to ensure a minimum particle size while recycling the large stuff back to the mill.

S. D. Pearson

SDP/elg/1937

Key Words: reaction rate, sucrose utilization, continuous technology

(26)

CONFIDENTIAL

RETENTION LIMIT: 1/1/96

CHEMICALS PRODUCT DEVELOPMENT DIVISION - OLESTRA PROCESS MONTHLY REPORT

S. D. PEARSON

FOR PERIOD ENDING 1/1/90

Very fast reactions to high octaester conversions (99%) have been acheived at 35mmHg using a packed column reactor and filtration.

FG REACTION TECHNOLOGY

The pressures required for methanol removal, and hence high octaester conversions, in either the batch or continuous stirred tank esterification reactors have typically been in the 1.0 mmHg - 3.0 mmHg range. Although we have demonstrated that higher pressures are feasible, this has always meant a significant increase in reaction time which can potentially lead to product color problems. In an effort to better understand our methanol transport limitations, Gene Hawkins and I have set up a lab packed column reactor in which the esterification reaction can be run (thanks to Ross Rieke for his input and many helpful suggestions and to Bob Gilbert for allowing us to modify his fatty acid column).

The system is configured so that it can handle up to 2 liters of crude, has a variable-flow external reflux line to introduce the crude back into the top, and can be nitrogen sparged from the bottom. The column is packed with three feet of Sulzer wire gauze. Temperature is controlled using heating tape on the recirculation line and pressure is primarily controlled through the sparge. For a typical experiment the crude is first reacted in a batch reactor through an extended stage I and then filtered to remove residual sucrose, catalyst, and the bulk of the soap. At this point the filtrate is transferred to the packed column where the reflux rate, temperature, sparge rate and pressure are set according to the experimental plan.

To date we have had extremely encouraging results, including: at a column pressure of 25mmHg at the top and 45mmHg at the bottom we have reacted to 99% octaester in less than two hours. In other words, we have been able to increase the operating pressure by at least an order of magnitude through more efficient methanol removal, without increasing the reaction time. I believe two things are contributing to these remarkable results. First, the packed column is probably supplying a larger surface area for mass transfer than we get in the batch or stirred tank reactors. Second, in filtering out the residual solids and soap we dramatically reduce the viscosity of the crude which can directly translate into higher methanol mass transfer coefficients.

We are continuing experiments in this area and I expect we will continue to see fast reactions at even higher operating pressures. Additionally, with the fast reaction rates we have been attaining in the packed column other operating conditions may become even more feasible, such as very low temperatures or low ester to sucrose ratios.

Scott D Pearson

S. D. Pearson

SDP/elg/2397

Keywords: packed column, filtration

(27)

LABORATORY BOOK NO. S1 6051

ASSIGNED TO D. P. Hawkins

TRANSFERRED TO SD. Reardon 4/20/90 DATE

CORRESPONDING LOOSE-LEAF NOTEBOOK _____

DATE ISSUED 9-15-89

DATE RETURNED 2.19.91

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B. Describe the purpose of the work, give a narrative description of what was done, and indicate the sequence in which each step was taken. Cross Reference data entries as appropriate for maximum clarity. For example, if analytical results on coded samples are entered in the notebook, enter the notebook and page number where the sample description can be found and provide references to procedures or analytical methods used.

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6

Date 1-8-90

Subject FG-BASE - STAGE II PACKED COLUMN REACTION STUDY

STAGE II PACKED COLUMN REACTION

This is to document initial work done by the undersigned to investigate FG-Base Stage II reaction rate in a packed column environment.

GENERAL

Jerry Lowder 1-8-90

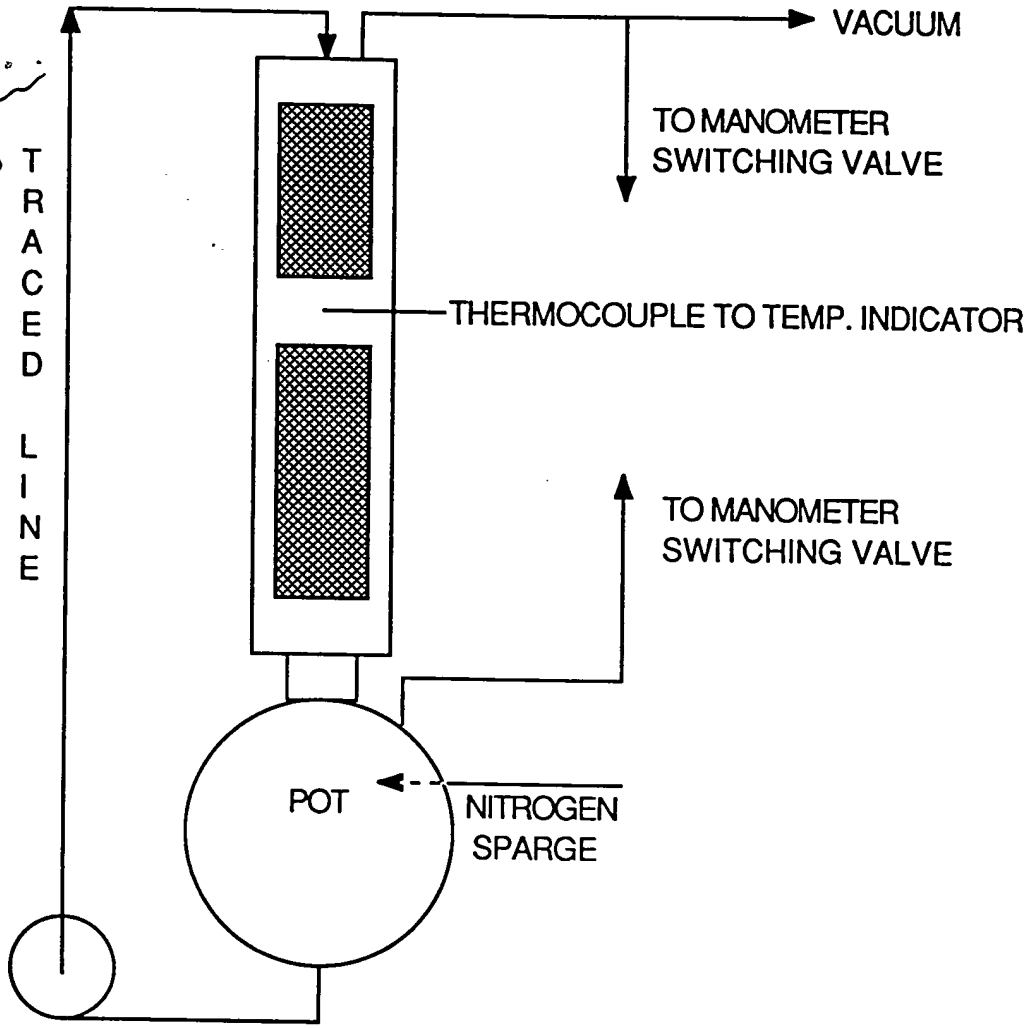
The runs described below were conducted in the following manner: all Stage I reactions were carried out in a batch system. The first run provided 1000 grams of Stage I material; this proved to be too little to keep the column and pump in equilibrium for Stage II reaction. A 1500-gram batch was made for the second run; this still wasn't quite enough to allow for product retention in the packing. All the rest of the runs were made at 2000-gram levels, which seemed to be marginally enough to keep the system fed. Stage I was run for about two hours at 275F and 1mm Hg in all cases, after which the Stage II esters and catalyst were added. When this material became turbid after about 1 - 1.5 hours of reaction, it was filtered for soap removal through two layers of fiberglas filter disc into the feed pot at the bottom of the column, and sampled. The charge was then brought up to temperature (275F) and pumped to the top of the column for recycle circulation through the packing under the desired conditions of vacuum and nitrogen sparge. Parametric particulars appear later in this summary.

r's Signature Jerry Lowder Date 1-8-90

orroborating Witness Scott D. Rea Date 1-8-90

Date

Subject



TRACED LINE

1-8-90

COLUMN AND PACKING

The column was set up as illustrated, utilizing cylindrical stainless mesh packing of 1 7/8" diameter. The top segment of the packing was 15" in length, the bottom segment 20". Nitrogen sparge was fed to the pot as noted. Vacuum level was monitored at both the pot and column top during the first two sets of conditions,

Worker's Signature [signature] Date 1-5-90

Corroborating Witness [signature] Date 1-8-90

Date 1-8-90

Subject

and at the top only during subsequent tests. Both points were monitored using a single manometer and switching valve setup; the top vacuum reading indicates actual mm Hg pulled by the pump; the difference between the two readings is equal to the pressure drop across the column. In order to minimize product holdup or backflow in the column packing, vacuum in higher pressure runs was controlled at specific nitrogen sparge rates by bleeding air in at the base of the manometer; the air so admitted went directly to the vacuum source, and thus never contacted the reaction mass. Nitrogen sparge values in the following table are given as micrometer valve settings.

1-8-90

RUN #	DATE	Pt,mm Hg	Pb,mm Hg	TEMP., F	SPA
1	12/11/89	15	35	275	0
2	12/15/89	25	45	260-284	:
3	12/28/89	44	*	273	;
"	"	"	*	"	•
4	1/3/90	75	*	275	;
"	"	"	*	"	•
"	"	"	*	"	•
"	"	"	*	"	•
5	1/4/90	100	*	275	;
"	"	"	*	"	•
"	"	"	*	"	•

*NOT READ

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Corroborating Witness [signature] Date 1-5-90

Date

Subject

EQUIPMENT LOG

PUMP CONTROLLER AND MOTOR : Cole Parmer 7144-04, 115VAC

PUMP HEAD : Cole-Parmer 7002-27, Gear type, 756 ml/min.

NITROGEN SPARGE FLOW VALVE : Nupro SS-4BMRW, operated at 10 psig head press

1-8-90

SPARGE	TIME, HRS.	OCTA	NOTES
0.8	2.00	99.2	@ START OF TURBID PHASE
2	1.50	99.0	@ START OF TURBID PHASE
2	0.75	91.1	~1/3 SOAP REMOVED
"	1.50	96.2	~1/3 SOAP REMOVED
2	0.75	42.2	TIME AFTER FILTRATION
"	1.50	73.8	TIME AFTER FILTRATION
"	2.00	84.9	TIME AFTER FILTRATION
"	2.50	87.3	TIME AFTER FILTRATION
2	1.00	47.9	TIME AFTER FILTRATION
"	2.00	54.1	TIME AFTER FILTRATION
"	3.00	58.4	TIME AFTER FILTRATION

1-8-90

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Corroborating Witness _____ Date 1-8-90

(28)

LABORATORY BOOK NO. SI 1384

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B. Describe the purpose of the work, give a narrative description of what was done, and indicate the sequence in which each step was taken. Cross Reference data entries as appropriate for maximum clarity. For example, if analytical results on coded samples are entered in the notebook, enter the notebook and page number where the sample description can be found and provide references to procedures or analytical methods used.

C. Define trade-named materials, acronyms or jargon, the first time they are used. Show the mathematical formula for all calculations and a sample calculation if the principle is not obvious. Computer programs used for data analysis should be referenced.

D. Enter factual results only. These include data as well as observations. Opinions should not be recorded in the notebook. Comments implying failure should be avoided.

E. Make entries on a given subject on consecutive pages where practical. Restrict each page to a single subject or test. When considerable work on a single subject is to be done, reserve a single notebook for the work whenever practical.

F. Do not skip pages. When unavoidable, cross through blank page(s) in ink, initial and date. Blank partial pages should also be crossed through in ink, initialed and dated.

G. Do not erase or use correction fluid in notebooks. When corrections are necessary:
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ATTACHMENTS

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C. FOLD-OUT ATTACHMENTS AND OVERLAPPING ATTACHMENTS ARE STRICTLY PROHIBITED.

SIGNATURES AND DATES

A. Minimum patentability standards require each notebook page to have two signatures: The person doing the work and a corroborating witness. A corroborating witness must be an unbiased non-inventor who preferably witnessed performance of the work in its entirety. The person doing the work must sign and date each notebook page.

B. Good Laboratory Practices (GLP's) require all entries on a page that are made on a date other than the date at the top of the page to show the current date and initials of the person making the entry.

C. Good Manufacturing Practices (GMP's) require production records to be signed by the person doing the work and by an independent observer. Laboratory Control records are required to be dated and signed by the person doing the work and by the person reviewing the records.

RESPONSIBILITY

A. The person to whom this book is issued is responsible for returning it to issuing Library as soon as it is no longer in active use.

B. Incomplete notebooks can be transferred to another person if both parties agree to the transfer and certify the transfer with the Files Clerk at the issuing Library.

C. This notebook must be indexed and have keywords assigned by the user before return to the Library. It must also include explicit cross-reference to all other notebooks loose-leaf and hardbound which contain related work.

34 Date 9-5-89

Subject F6 Base

Preparation of feed mix

Soap: Add 393g I-1 Ester to feed tank. Dissolve 75g of KOH in 1310g methanol then add to esters. Reflux for 4 hours. Makes 425g of Soap

Catalyst: Grind ~~50~~ 25g of K_2CO_3

Sucrose: Milled and sieved to <63 microns
1136g of sucrose collected

Esters: 5343g of 18-2 Methyl Esters

The methanol was taken off overnight after the esters were added. The following day, the sucrose was added and allowed to recirculate until the next morning.

TOTAL AMOUNTS USED

425g of SOAP
1136g of <63 micron sucrose
5343g of 1372-18-2 Esters
25g of powdered K_2CO_3

Worker's Signature R S. Berger Date 9-5-89

Corroborating Witness _____ Date _____

Date 9-7-89

Subject FG Base

Continuous Run <63 micron sucrose

1000g of feed reacted batchwise for 1.5 hrs, then feed turned on at 30 cycles per hour. Pressure at 15 mm Hg.

Time		Temp°C	Pressure mm Hg	
8:35		135	15	
8:50		135	15	
9:05		133	15	
9:35		135	15	
10:05	SAMPLED	135	15	
10:35		134	15	
11:05	SAMPLED	134	15	
11:35		135	15	
12:05	SAMPLED	135	15	
12:35		135	15	
1:05	SAMPLED	135	15	
1:35		134	15	
2:05	SAMPLED	135	15	
2:35		135	15	
3:05	SAMPLED	135	15	
3:35		135	15	6.5hrs Reaction stopped- vac. off - nitrogen on overnight
8:20	9/8	135	15	Feed started - back to temp- vac. on
8:50	SAMPLED	135	15	
9:20		135	15	
9:50	SAMPLED	135	15	
10:20		134	15	
10:50	SAMPLED	134	15	
11:20		135	15	
11:50	SAMPLED	135	15	
12:20		134	15	
12:50	SAMPLED	134	15	RUN ENDED

Data next page

Worker's Signature G. S. Berger Date 9-7-89

Corroborating Witness _____ Date _____

36

Date 9-8-89

Subject F6 Base

Data from page 35

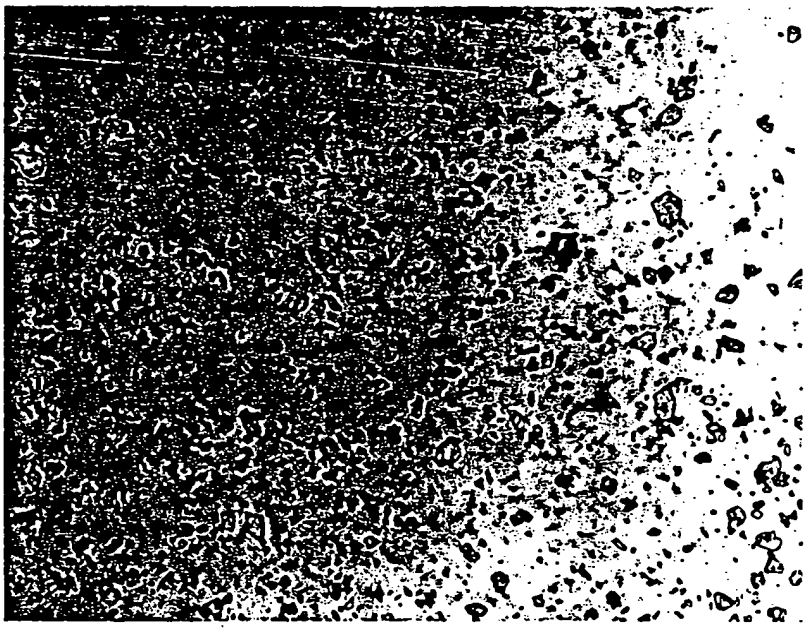
1372-18-2 Esters + <63 micron sucrose

HRS	1	2	3	4	5	6	7	8	I-BAR	SUCROSE
1.5	28.6	33.6	22.8	9.4	4.1	1.4			1.97	12.31
2.5	17.7	29.0	28.1	15.7	7.0	2.6			2.34	8.07
3.5	15.8	21.3	27.0	18.4	10.1	5.4	2.0		2.59	5.95
4.5	11.1	22.3	27.0	19.9	10.6	6.3	2.8		2.77	5.11
5.5	13.9	19.8	26.7	19.0	10.3	5.6	3.7	1.1	2.73	5.07
6.5	11.9	23.5	27.6	19.0	10.2	5.3	2.5		2.70	5.59
7.5	10.4	21.9	27.8	20.3	11.5	5.6	2.4		2.80	4.15
8.5	10.6	22.4	27.5	19.7	11.0	5.8	2.7	0.2	2.79	4.53
9.5	11.7	22.9	28.4	19.9	10.6	5.2	1.2		2.70	4.76
10.5	10.4	22.1	27.5	20.1	11.4	6.0	2.5		2.80	4.23
11.5	9.7	21.9	28.3	21.2	11.9	5.6	1.4		2.81	3.08

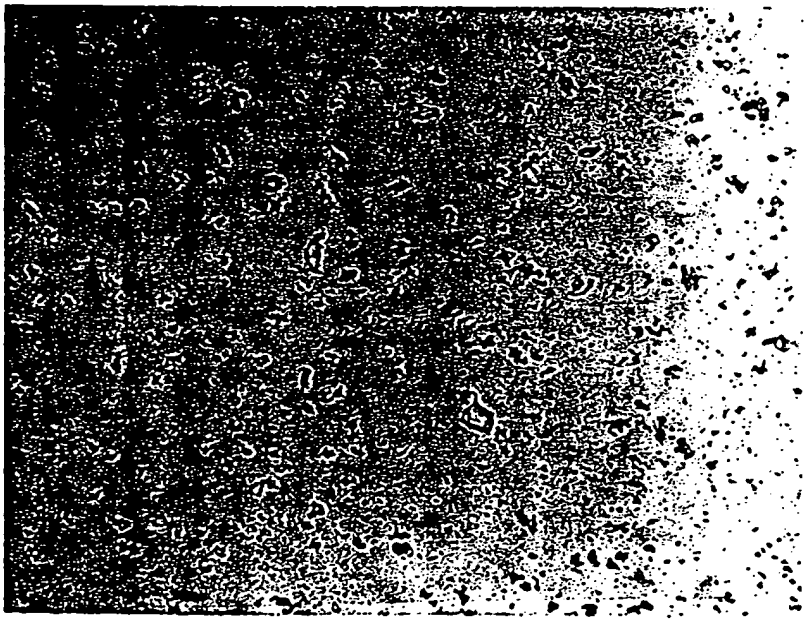
Worker's Signature R. S. Berger Date 9-8-89

Corroborating Witness _____ Date _____

Subject



463 MICRON SLURRY (SIEVED) 1384-34
B. HUNTER 9-15-89 10X



FEED MADE FROM 463 MICRON SLURRY (SIEVED)
B. HUNTER 9-15-89 10X 1384-34

Worker's Signature _____ Date _____

Corroborating Witness _____ Date _____

38 Date 9-19-89

Subject FG Base

Preparation of feed mix

Soap: Add 393 g I-1 Esters to feed tank. Dissolve 75g of KOH completely in 1310 g of methanol. Then add the KOH/Methanol to the esters and reflux at 60-65°C for 4 hours. This makes 425g of soap.

Sucrose: Milled and sieved to < 38 microns
1136g needed

Catalyst: Grind by hand 25g of K_2CO_3

Esters: 5350g of 1372-18-3 Methyl Esters

The methanol was taken off after adding the esters, then the catalyst was added. The sucrose was then added and allowed to recirculate for 1.5 hours.

TOTAL AMOUNTS USED

425 g SOAP
25 g K_2CO_3 (powdered)
5350g 1372-18-3 Methyl Esters
1136g of < 38 micron sucrose

Worker's Signature R. S. Berger Date 9-19-89

Corroborating Witness Date

Date 9-20-89

Subject EG Base

Continuous Run < 38 micron sucrose

1000g of feed added to the reactor, vac turned on to 15mmHg, temp raised to 135°C and reacted for 1.5 hrs. Then feed turned on at 30 cycles per hour.

TIME		TEMP°C	PRESSURE mmHg	
11:00		135	15	
11:30		135	15	
12:00		135	15	
12:30	SAMPLED	135	15	FEED STARTED
1:00		135	15	
1:30	SAMPLED	135	15	
2:00		134	15	
2:30	SAMPLED	135	15	
3:00		135	15	
3:30	SAMPLED	136	15	Vac. off - nitrogen on overnight
8:00	9/21			Vac. on - back up to temp - feed restarted

Level of reactor was full because feed valve did not close, therefore run was terminated

< 38 micron sucrose

HRS	1	2	3	4	5	6	7	8	I-BAR	SUCROSE
1.5	31.3	34.0	21.3	8.8	3.6	1.0			1.90	8.35
2.5	14.2	24.8	26.1	16.0	9.3	5.5	2.6	1.7	2.62	6.52
3.5	10.4	24.1	29.9	19.3	9.5	4.5	1.6	0.7	2.72	4.73
4.5	8.9	19.7	26.4	20.4	12.8	7.9	3.3	0.8	2.97	3.78

Worker's Signature R. S. Berger Date 9-20-89

Corroborating Witness _____ Date _____

(29)

LABORATORY BOOK NO. SI 6044 CORRESPONDING LOOSE-LEAF NOTEBOOK

DATE ISSUED 1-17-89

ASSIGNED TO P. J. Corregan

DATE RETURNED 11-24-93

TRANSFERRED TO R. S. Berger 3.26.90
DATE

BS
S.W.T.C.

INSTRUCTIONS FOR ENTERING DATA IN LABORATORY NOTEBOOKS.

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Date 11-3-89

Subject FG Base

Amt. of Catalyst

108g of 1372-18-3 esters added to reactor. 9g of K⁺ soap, 25g of powdered (C+H) sucrose + 0.5g of powdered K_2CO_3 add for Stage 1. After 1.5hrs 64.8g of esters + 0.5g of K_2CO_3 (powd) were added.

TIME	TEMP °C	PRESSURE mmHg	
8:40	135	0.9	
8:55	135	1.0	
9:10	135	1.3	
9:25	135	1.2	
9:40	135	1.0	
9:55	135	1.0	
10:10 SAMPLED	135	1.0	
10:15	135	0.9	BACK UP TO TEMP
10:45	135	1.3	
11:15 SAMPLED	135	2.1	
11:45	135	2.5	
12:15 SAMPLED	135	1.9	
12:45	135	1.6	
1:15 SAMPLED	135	1.0	
1:45	135	0.8	
2:15 SAMPLED	135	0.7	
END			

DFK (ppm)	HRS	1	2	3	4	5	6	7	8.	I-BAR	SUCROSE
16	1.5	30.9	36.6	23.2	9.3					1.85	8.04
41	2.5	13.4	27.9	26.5	13.3	9.4	8.5	1.1		2.58	2.92
37	3.5		1.4	6.1	14.5	18.6	23.3	25.9	10.3	5.39	0.23
	4.5					11.2	18.2	35.6	35.1	6.81	—
121	5.5						0.8	35.2	64.0	7.60	—

Worker's Signature R L Berger Date 11-3-89

Corroborating Witness R W. Mann Date 7/29/93

90 Date 11-6-89

Subject FG Base

Amt. of Catalyst

Stage 1: 108g of 1372-18-3 Esters, 9g of K^+ soap, 25g of (powd) sucrose, 1.0g K_2CO_3 (powd)

After 1.5 hours, Stage 2: Add 64.8g of esters + 1.0g of (powd) K_2CO_3.

TIME	TEMP °C	PRESSURE mmHg	
8:10	135	1.0	
8:25	135	0.9	
8:40	135	0.9	
8:55	135	1.0	
9:10	135	1.0	
9:25	135	1.0	
9.40 SAMPLED	135	1.2	
9:45	135	1.3	
10:15	135	2.2	
10:45 SAMPLED	135	2.6	
11:15	135	2.0	
11:45 SAMPLED	135	1.8	
12:15	135	1.5	
12:45 SAMPLED	135	0.9	
1:15	135	0.8	
1:45 SAMPLED	135	0.7	Run Ended

DFK (ppm)	HRS	1	2	3	4	5	6	7	8	I-BAR	SUCROSE
28	1.5	17.3	32.9	27.1	22.6					2.25	4.46
35	2.5	2.6	22.3	15.5	11.0	12.8	17.4	13.6	5.0	3.66	0.88
68	3.5			1.7	7.3	18.2	28.3	31.2	13.3	5.98	0.26
109	4.5				1.6	17.0	22.7	32.3	26.4	6.49	0.0
90	5.5					9.8	18.6	34.5	37.1	6.86	0.0

Worker's Signature R S Berger Date 11-6-89

Corroborating Witness B W. Mason Date 2/29/93

Date 11-7-89

Subject FG Base

Amt. of Catalyst

Stage 1: 0.25g of K_2CO_3 (powd) used with 108g of 1372-18-3 Esters, 9g of K^+ soap, and 25g of powd sucrose. After 1.5 hours add 0.25g of K_2CO_3 and 64.8g of esters

TIME	TEMP °C	PRESSURE mmHg	
8:15	135	0.8	
8:30	135	0.7	
8:45	135	0.7	
9:00	135	0.7	
9:15	135	0.7	
9:30	135	0.6	
9:45 SAMPLED	136	0.7	
9:50	135	0.9	Back up to temp.
10:20	135	0.9	
10:50 SAMPLED	135	1.2	
11:20	135	1.8	
11:50 SAMPLED	135	1.9	
12:20	135	1.9	
12:50 SAMPLED	135	1.7	
1:20	135	1.4	
1:50 SAMPLED	135	1.2	Run Ended

DEX (ppm)	HRS	1	2	3	4	5	6	7	8	I-BAR	SUCROSE
20	1.5	50.2	34.7	12.9	2.2					1.49	7.75
28	2.5	24.2	28.9	21.0	11.9	8.8	5.3			2.20	4.88
22	3.5	8.6	23.4	28.7	19.1	10.5	7.2	2.5		2.65	1.28
30	4.5		2.5	9.2	16.4	23.1	25.0	19.0	4.9	4.99	0.27
29	5.5				4.2	15.2	28.2	35.6	16.8	6.29	0.38

Worker's Signature R S Berger Date 11-7-89

Corroborating Witness D W. Mar Date 7/29/93

92 Date 11-8-89

Subject FG Base

Amt. of Soap

108g of 1372-18-3 Esters, 0.5g of K_2CO_3 (powd), .25g of powd. sucrose & 6g of K^+ soap in stage 1. After 1.5hrs add 64.8g of esters & 0.5g K_2CO_3.

TIME		TEMP°C	PRESSURE mmHg	
8:35		135	1.3	
8:50		135	1.6	
9:05		135	1.6	
9:20		135	1.6	
9:35		135	1.7	
9:50		135	1.8	
10:05	SAMPLED	135	1.8	
10:10		135	2.1	
10:40		135	2.0	
11:10	SAMPLED	135	2.2	
11:40		135	2.3	
12:10	SAMPLED	135	2.5	
12:40		135	2.3	
~~12:~~ 1:10	SAMPLED	135	2.1	
1:40		135	2.0	
2:10	SAMPLED	135	1.7	Run Ended

DFK (ppm)	HRS	1	2	3	4	5	6	7	8	I-BAR	Sucrose
24	1.5	36.4	36.2	22.8	4.6					1.73	14.12
47	2.5	11.6	20.4	25.1	19.3	14.1	7.4	2.0		2.82	5.59
24	3.5	1.0	5.8	15.1	20.3	23.5	21.6	11.1	1.6	4.33	0.25
46	4.5			2.1	21.8	23.1	21.2	19.3	12.6	5.43	0.0
61	5.5				3.6	11.4	23.5	36.2	25.4	6.52	0.0

Worker's Signature R S Berger Date 11-8-89

Corroborating Witness D W. Mason Date 7/29/93

Date 11-10-89

Subject FG Base

Amt of Soap

108g of 1372-18-3 Esters, 0.5g K_2CO_3 (powd), 25g of powd. sucrose & 12g of K^+ soap. added in stage 1. After 1.5 hours add 64.8g of esters + 0.5g K_2CO_3.

TIME		TEMP°C	PRESSURE mmHg	
8:30		135	1.3	
8:45		135	1.1	
9:00		135	1.1	
9:15		135	1.1	
9:30		135	1.1	
9:45		135	1.2	
10:00	SAMPLED	135	1.2	
10:10		135	1.3	
10:40		135	1.9	
11:10	SAMPLED	135	2.0	
12:10	SAMPLED	135	1.9	
12:40		135	1.7	
1:10	SAMPLED	135	1.6	
1:40		135	1.5	
2:10	SAMPLED	135	1.2	Run Ended

DFK ppm	HRS	1	2	3	4	5	6	7	8	I-BAR	SUCROSE
17	1.5	52.5	31.7	12.3	3.5					1.48	7.75
20	2.5	8.8	20.3	28.1	19.7	12.8	8.4	2.0		2.92	1.67
32	3.5		2.6	9.8	17.6	21.5	21.7	18.6	7.9	4.98	0.16
	4.5				1.6	7.9	19.9	35.9	34.7	6.80	0.14
86	5.5					4.1	12.5	31.3	52.1	7.21	0.0

Worker's Signature R S Berger Date 11-10-89

Corroborating Witness R W. Mason Date 7/29/93

96 Date 11-15-89

Subject F6 Base

Amt of catalyst

Repeat of page 90: 108g 1372-18-3 esters, 25g of powd sucrose, 9g K^+ soap + 1.0g K_2CO_3 in stage 1: After 1.5 hrs 64.8g of esters + 1.0g K_2CO_3 added.

TIME		TEMP°C	PRESSURE mmHg	
8:10		135	0.8	
8:25		135	0.8	
8:40		135	0.8	
8:55		135	0.9	
9:10		135	1.0	
9:25		135	1.2	
9:40	SAMPLED (1.5)	135	1.3	64.8g of esters + 1.0g K_2CO_3 added
9:50		135	1.2	
10:20		135	1.8	
10:50	SAMPLED (2.5)	135	2.1	
11:20		135	1.7	
11:50	SAMPLED (3.5)	135	1.2	
12:20		135	1.1	
12:50	SAMPLED (4.5)	135	1.0	
1:20		135	1.0	
1:50	SAMPLED (5.5)	135	09	Run Ended

↓

HRS	1	2	3	4	5	6	7	8	DFK	I-BAR sucrose		VFK
1.5	34.1	30.6	21.1	7.7	4.5	1.9				1.87	8.66	
2.5	1.1	7.1	16.0	22.9	19.9	18.6	12.2	2.3	22	4.23	6.49	22
3.5		0.3	1.3	5.0 ~~0.3~~	12.2	21.9	34.4	24.7	59	6.32	0.20	59
4.5				1.4	5.0	15.6	33.4	44.7	99	7.02	0.19	99
5.5				0.3	1.6	8.0	29.6	60.5	126	7.41	0.21	126

Worker's Signature R S Berger Date 11-15-89

Corroborating Witness D W. Mason Date 7/29/93

(30)

LABORATORY BOOK NO. SI 1384

ASSIGNED TO [illegible]

TRANSFERRED TO _____ DATE

_____

_____

CORRESPONDING LOOSE-LEAF NOTEBOOK _____

_____

_____

DATE ISSUED [illegible]

DATE RETURNED _____

SUBJECT _____

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76 Date 12-20-89

Subject FG Base

Feed mix Double Catalyst

Soap: Take 393g of I-1 Esters
75g of KOH
1310g of methanol
Reflux for 4 hours at 60-65°C

Catalyst: 50g of powd. K_2CO_3

Esters: 5350g of 1372-18-3 Methyl Esters

Sucrose: 1136g of sucrose powdered by jet mill at 3 lbs/hr

TOTALS

425g Soap

50g of powd. K_2CO_3

5350g of 1372-18-3 esters

1136g of jet milled sucrose 3 lbs/hr

Worker's Signature R S Berger Date 12-20-89

Corroborating Witness Date

78 Date 12-21-89

Subject EG Base

Double Catalyst Run

1000g of feed mix (pg76) reacted for 1.5 hours then feed turned on at 30 cycles per hour. Recirc. valve at 1¼ turn.

TIME		TEMP°C	PRESSURE mmHg
8:30		135	15
9:00		134	15
9:30		135	15
10:00	SAMPLE (1.5)	136	15
10:30		134	15
11:00	SAMPLE (2.5)	135	15
11:30		135	15
12:00	SAMPLE (3.5)	135	15
12:30		136	15
1:00	SAMPLE (4.5)	135	15
1:30		134	15
2:00	SAMPLE (5.5)	135	15
2:30		135	15
3:00	SAMPLE (6.5)	135	15

HRS	1	2	3	4	5	6	7	8	I-BAR	SUCROSE
1.5	28.9	37.6	23.4	10.1					1.89	6.07
2.5	10.0	22.3	28.4	19.6	10.4	9.4			2.80	1.56
3.5	6.4	18.0	28.0	22.9	12.5	9.9	2.3		3.10	0.81
4.5	4.8	17.6	27.6	24.2	13.8	7.1	3.6	1.2	3.20	0.63
5.5	4.0	17.1	28.2	23.8	12.7	8.9	5.3		3.27	0.64
6.5	3.1	15.3	28.2	25.1	15.0	7.7	5.5		3.37	0.42

Worker's Signature R S Berger Date 12-21-89

Corroborating Witness _____ Date _____

Date 12-27-89

Subject FG Base

Feed Mix Double Catalyst

Soap: 393g of I-1 Esters
75g of KOH
1310g of methanol
Reflux for 4 hours.

Catalyst: 50g of powdered K_2CO_3

Esters: 5350g of 1372-18-3 Methyl Esters

Sucrose: 1136g of jet milled sucrose at 3 lbs/hr

TOTAL

425g Soap

50g of powd. K_2CO_3

5350g of 1372-18-3 Esters

1136g of jet milled sucrose 3 lbs/hr

Worker's Signature R & C Berger Date 12-27-89

Corroborating Witness _____ Date _____

80

Date 12-28-89

Subject EG Base

1000g of feed mix from page 79 added to the reactor and reacted batchwise for 1.5 hours before turning on feed at 30 cycles per hour. Recirc valve at 1¼ turn.

TIME	TEMP°C	PRESSURE mmHg	
9:00	135	15	
9:30	134	15	
10:00	135	15	
10:30 SAMPLE (1.5)	135	15	Feed Started
11:00	135	15	
11:30 SAMPLE (2.5)	136	15	
12:00	135	16	
12:30 SAMPLE (3.5)	136	16	
1:00	135	16	
1:30 SAMPLE (4.5)	136	16	
2:00	135	15	
2:30 SAMPLE (5.5)	135	15	
3:00	135	15	
3:30 SAMPLE (6.5)	135	15	

HRS	1	2	3	4	5	6	7	8	I-BAR	Sucrose
1.5	25.8	32.5	24.9	11.7	5.1				2.04	8.01
2.5	16.6	29.9	28.9	15.8	6.6	2.3			2.35	4.95
3.5	11.3	24.0	27.9	18.9	9.4	6.5	2.0		2.71	2.04
4.5	9.4	21.4	28.0	20.7	10.8	7.9	1.9		2.86	1.13
5.5	8.9	23.7	32.0	22.5	9.7	3.1			2.74	1.03
6.5	9.7	23.0	30.5	22.4	10.5	3.2	0.7		2.74	1.00

Worker's Signature R S Berger Date 12-28-89

Corroborating Witness _____ Date _____

Date 12-29-89

Subject FG Base

1000g of feed mix (pg 79) reacted batchwise for 1.5 hours. then feed on at 30 cycles/hr. Recirc. line at 3/4 turn.

TIME		TEMP °C	PRESSURE mmHg
8:15		135	15
8:45		136	15
9:15		136	15
9:45	SAMPLE (1.5)	135	15
10:15		135	15
10:45	SAMPLE (2.5)	135	15
11:15		135	15
11:45	SAMPLE (3.5)	135	16
12:15		135	16
12:45	SAMPLE (4.5)	135	15
1:15		135	15
1:45	SAMPLE (5.5)	135	15
2:15		135	15
2:45	SAMPLE (6.5)	135	15

HRS	1	2	3	4	5	6	7	8	I-BAR	SUCROSE
1.5	19.0	30.1	28.0	14.4	6.2	2.3			2.28	7.05
2.5	12.9	24.3	27.5	18.2	8.9	6.0	2.2		2.64	3.14
3.5	9.5	21.8	28.9	21.4	10.4	6.2	1.8		2.82	1.15
4.5	8.8	22.0	30.1	21.7	10.2	4.3	3.0		2.84	0.71
5.5	6.9	19.3	30.0	24.1	13.2	4.6	1.8		2.98	0.76
6.5	7.6	18.3	28.5	24.0	13.4	6.2	2.1		3.00	0.61

Worker's Signature R S Berger Date 12-29-89

Corroborating Witness _____ Date _____

(31)

LABORATORY BOOK NO. SI 6055
ASSIGNED TO P. J. Corrigan
TRANSFERRED TO R. S. Berger 3/26/90 DATE

CORRESPONDING LOOSE-LEAF NOTEBOOK _____

DATE ISSUED 11-14-89
DATE RETURNED 11-10-93
SUBJECT _____
BS
S.W.T.C.

INSTRUCTIONS FOR ENTERING DATA IN LABORATORY NOTEBOOKS.

LABORATORY NOTEBOOKS ARE LEGAL DOCUMENTS. NOTEBOOKS NOT COMPLYING WITH SPECIFICATIONS MAY BE RETURNED FOR CORRECTION. SEE "A GUIDE TO THE USE OF LABORATORY NOTEBOOKS" FOR ADDITIONAL INFORMATION.

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24 Date 2-7-90

Subject FG Base

Nitrogen Sparge in stage II at 15mmHg

Stage 1: Standard conditions; 144g 1395-39 Esters, 24g kt soap, 34.4g Sucrose + 1.4g K_2CO_3. Raise temp to 135°C + hold pressure at 15mmHg.

Stage 2: Add 205g Esters + 1.4g K_2CO_3. Hold pressure at 15 mmHg. Sparge with nitrogen flow at 20-30 babbing

TIME	TEMP°C	PRESSURE mmHg	
7:55	135°C	15	
8:25	135	15	
8:55	135	15	
9:25 SAMPLE (1.5)	135	15	205g of ester + 1.4g K_2CO_3 - nitrogen sparge on.
9:35	135	15	
10:05	135	15	
10:35 SAMPLE (2.5)	135	15	
11:05	135	15	
11:35 SAMPLE (3.5)	135	15	
12:05	135	15	
12:35 SAMPLE (4.5)	135	15	
1:05	135	15	
1:35 SAMPLE (5.5)	135	15	
2:05	135	15	
2:35 SAMPLE (6.5)	135	15	Run Ended

HRS	1	2	3	4	5	6	7	8	I-BAR	Sucrose	DFK
1.5	29.2	39.3	24.7	6.7					1.85	1.98	
2.5				1.0	7.2	16.1	33.9	41.9	6.95	0.03	
3.5					1.7	8.0	25.2	65.1	7.46	—	138
4.5						4.1	17.4	78.4	7.70	—	304
5.5					"	4.0	12.0	84.0	7.76	—	305
6.5						1.9	7.9	90.3	7.86	—	308

Worker's Signature R S Berger Date 2-7-90

Corroborating Witness B W. Mann Date 7/27/93

Date 2-8-90

Subject Stage 2 at 25mm Hg and ultrasound & nitrogen sparge

Stage 1: Standard conditions 146g 1395-39 esters, 24g Kt soap, 34.4g sucrose & 1.4g K_2CO_3. Raise temp to 135°C & hold pressure at 15mmHg

Stage 2: Add 205g esters & 1.4g K_2CO_3. Hold pressure at 25 mmHg ultrasound at an output of 60 (50 switch) & Nitrogen flow at 20.

TIME	TEMP°C	PRESSURE mmHg	
8:05	135	15	
8:35	135	15	
9:05	135	15	
9:35 SAMPLE (1.5)	135	15	205g esters & 1.4g K_2CO_3 - ultrasound on nitrogen sparge on
9:45	135	25	
10:15	135	25	
10:45 SAMPLE (2.5)	135	25	
11:15	135	25	
11:45 SAMPLE (3.5)	135	25	
12:15	135	25	
12:45 SAMPLE (4.5)	135	25	
1:15	135	25	
1:45 SAMPLE (5.5)	135	25	
2:15	135	25	
2:45 SAMPLE (6.5)	135	25	

HRS	1	2	3	4	5	6	7	8	T-BAR	SUCROSE	DFK
1.5	23.9	39.3	25.4	11.4					1.99	1.25	
2.5			0.8	3.2	9.9	22.9	37.1	26.2	6.53	0.07	
3.5				2.5	4.1	12.2	30.6	50.6	7.08	—	
4.5					0.9	5.0	22.6	71.5	7.59	—	204
5.5						1.9	12.4	85.7	7.81	—	251
6.5						1.2	10.4	88.4	7.85	—	263

Worker's Signature R J Berger Date 2-8-90

Corroborating Witness [illegible] Mason Date 7/27/93

28 Date 2-13-90

Subject Fa Base

Dropwise addition of stage 2 esters along with nitrogen sparge. +15MM

Standard conditions in stage 1 : 146g (1315-39) esters, 34.4g sucrose, 24g K+soap + 1.4g K_2CO_3

Stage 2 : Add 1.4g K_2CO_3 and 205g of esters dropwise

Turn on nitrogen sparge and keep pressure at 15mmHg

TIME		TEMP °C	PRESSURE mmHg	
8:00		135	15	
8:30		135	15	
9:00		135	15	
9:30	SAMPLE (1.5)	135	15	205g ester add dropwise, 1.4g K_2CO_3 added
10:00		135	15	
10:30	SAMPLE (2.5)	135	15	
11:00		135	15	
11:30	SAMPLE (3.5)	135	15	
12:00		135	15	
12:30	SAMPLE (4.5)	135	15	
1:00		135	15	
1:30	SAMPLE (5.5)	135	15	
2:00		135	15	
2:30	SAMPLE (6.5)	135	15	Ester all in at 2:25
3:00		135	15	
3:30	SAMPLE (7.5)	135	15	Run Ended

HRS	1	2	3	4	5	6	7	8	I.BAR	SUCROSE	DFK	%ME
1.5	24.2	38.4	24.0	11.4					1.94	1.30		
2.5	0.8	6.6	18.9	29.0	24.3	16.6	2.2	1.6	4.02	—		23.8
3.5		1.7	7.4	20.1	26.3	22.4	14.8	7.2	5.01	—		17.6
4.5			1.4	8.6	19.3	25.3	28.8	16.6	5.98	—		25.7
5.5				1.3	7.2	18.5	39.0	34.1	6.84	—		34.1
6.5						9.1	35.6	55.3	7.40	—	55	36.7
7.5						2.3	23.5	74.2	7.68	—	75	34.6

Worker's Signature R S Berger Date 2-13-90

Corroborating Witness B W. Mann Date 7/27/93

32 Date 2-20-90

Subject FG Base

Dropwise addition of stage 2 esters at 25 mm Hg/Nitrogen sparge (5h

Run stage 1 at standard conditions: 146g ester (1395-39), 24g K^+ soap, 34.4g sucrose + 1.4g K_2CO_3

Pressure controlled at 15 mm Hg. Add 205g of esters dropwise over

and hold pressure at 25 mm Hg. Add 1.4g K_2CO_3 before starting addition.

Sparge with nitrogen in Stage 2.

TIME		TEMP°C	PRESSURE mm Hg	
8:00		135	15	
8:30		135	15	
9:00		135	15	
9:30	SAMPLE (1.5)	135	15	1.4g K_2CO_3 added
9:35		135	25	205g esters added dropwise
10:05		135	25	Stirr speed ~600 rpm
10:35	SAMPLE (2.5)	135	25	← Nitrogen sparge on at flow of 20
11:05		135	25	
11:35	SAMPLE (3.5)	135	25	
12:05		135	25	
12:35	SAMPLE (4.5)	135	25	
1:05		135	25	
1:35	SAMPLE (5.5)	135	25	
2:05		135	25	
2:35	SAMPLE (6.5)	135	25	2:30 all esters in.
3:05		135	25	
3:35	SAMPLE (7.5)	135	25	Reaction stopped nitrogen on & cooled overnight
7:50	2/21	135	25	Restarted
8:20		135	25	
8:50	SAMPLE (8.5)	135	25	
9:20		135	25	
9:50	SAMPLE (9.5)	135	25	
10:20		135	25	
10:50	SAMPLE (10.5)	135	25	
11:20		135	25	
11:50	SAMPLE (11.5)	135	25	

Worker's Signature R S Bergen Date 2-20-90

Corroborating Witness B W. Mason Date 2/28/93

Date 2-21-90

Subject EG Base

(Shig) Cont. from last page

TIME		TEMP°C	PRESSURE mmHg
12:20		135	25
12:50	SAMPLE (12.5)	135	25
1:20		135	25
1:50	SAMPLE (13.5)	135	25

HRS	1	2	3	4	5	6	7	8	I-BAR	SUCROSE	DEX	TME
1.5	30.5	36.6	24.1	8.4	0.3				1.86	2.12		53.8
2.5	2.0	9.6	21.7	28.9	20.2	10.9	4.6	2.0	3.75	0.05		37.5
3.5			9.2	19.8	24.0	24.8	16.4	5.6	5.07	—		34.3
4.5			3.6	9.5	17.9	24.9	27.4	16.6	5.85	-		34.5
5.5				2.7	8.8	21.8	35.2	31.5	6.68	—		25.9
6.5					6.0	16.8	30.8	46.4	7.06	—		45.9
7.5						6.9	27.5	65.6	7.54	—	162	37.3
8.5						1.9	20.2	77.9	7.73	—	208	38.6
9.5						3.3	14.7	82.0	7.75	—	224	38.2
10.5						3.1	15.2	81.7	7.75	—	192	39.4
11.5						2.9	12.1	85.0	7.79	—	246	39.3
12.5						1.5	12.5	86.0	7.82	-	228	37.5
13.5						2.3	12.0	85.7	7.81	—	243	48.2

Worker's Signature R S Berger Date 2-21-90

Corroborating Witness B W. Mase Date 7/28/93

Date 3-9-90

Subject EG Base

30 mm + N_2 sparge in stage 2

Run standard conditions in stage 1 : 146g (1345-39) esters, 34.4g sucrose, 24g K+ soap + 1.4g K_2CO_3. In stage 2 add 205g esters + 1.4g K_2CO_3 and Sparge with nitrogen at 30 mm Hg.

TIME		TEMP°C	PRESSURE mmHg	
8:00		135	15	
8:30		135	15	
9:00		135	15	
9:30	SAMPLE (1.5)	135	15	~205g esters + 1.4g K_2CO_3
9:40		135	30	(Nitrogen on flow rate & bubbling up to 30)
10:10		135	30	
10:40	SAMPLE (2.5)	135	30	
11:10		135	30	
11:40	SAMPLE (3.5)	135	30	
12:10		135	30	
12:40	SAMPLE (4.5)	135	30	
1:10		135	30	
1:40	SAMPLE (5.5)	135	30	
2:10		135	30	
2:40	SAMPLE (6.5)	135	30	
3:10		135	30	
3:40	SAMPLE (7.5)	135	30	Run Ended

HRS	1	2	3	4	5	6	7	8	T-BAR SUCROSE	DFK		screening base
1.5	14.7	31.3	33.0	16.8	3.0	1.2			2.35	1.11		0.246 meq/g
2.5			2.3	7.3	16.7	24.2	30.3	19.1	6.05	0.08		0.00101 meq/g
3.5					1.8	12.0	35.5	50.7	7.27	—		
4.5						8.0	31.9	60.1	7.46	—	94	
5.5						4.8	32.5	62.7	7.53	—	93	
6.5						5.0	26.8	68.2	7.59	—	106	
7.5						5.1	23.9	71.0	7.61	—	96	

Worker's Signature R S Berger Date 3-9-90

Corroborating Witness B O W. Mann Date 7/28/93

46 Date 3-12-90

Subject FG Base

45 mm Hg + N_2 sparge in Stage 2

Stage 1 run at standard conditions: 15 mm Hg, 146g esters (1395-39), 34.4g sucrose (fondant), 24g K+ soap + 1.4g K_2CO_3. Stage 2 add 205g esters + 1.4g K_2CO_3 and a pressure of 45 mm with nitrogen sparge. Flow rate bubbling up to 30.

TIME		TEMP°C	PRESSURE mmHg	
7:55		135	15	
8:25		135	15	
8:55		135	15	
9:25	SAMPLE (1.5)	135	15	205g esters + 1.4g K_2CO_3
9:35		135	45	
10:05		135	44	
10:35	SAMPLE (2.5)	135	46	
11:05		135	46	
11:35	SAMPLE (3.5)	135	44	
12:05		135	44	
12:35	SAMPLE (4.5)	135	44	
1:05		135	44	
1:35	SAMPLE (5.5)	135	43	
2:05		135	45	
2:35	SAMPLE (6.5)	135	45	
3:05		135	45	
3:35	SAMPLE (7.5)	135	45	Nitrogen on overnight.

TIME		TEMP°C	PRESSURE mmHg	
8:00	3/13	135	45	Restarted
8:30		135	44	
9:00	SAMPLE (8.5)	135	46	
9:30		135	45	
10:00	SAMPLE (9.5)	135	46	
10:30		135	45	
11:00	SAMPLE (10.5)	135	46	
11:30		135	44	
12:00	SAMPLE (11.5)	135	43	
12:30		135	44	
1:00	SAMPLE (12.5)	135	43	INCREASED N_2 FLOW
1:30		135	45	steady at 30
2:00	SAMPLE (13.5)	135	45	
2:30		135	45	
3:00	SAMPLE (14.5)	135	46	Run Ended

Worker's Signature R S Berger Date 3-12-90

Corroborating Witness B W. Marr Date 7/28/93

Date 3-13-90

Subject F6 Base

DATA FROM LAST PAGE (46)

HRS	1	2	3	4	5	6	7	8	IBAR	SUCROSE	DEV
1.5	23.8	35.0	26.8	11.4	3.0				2.05	1.80	—
2.5		0.8	7.5	16.3	20.6	22.0	21.8	11.0	5.29	—	—
3.5			1.3	4.4	11.4	23.8	34.0	25.0	6.39	—	—
4.5				4.6	6.1	15.8	32.5	41.0	6.81	—	—
5.5						8.6	32.9	58.5	7.44	—	—
6.5						2.1	29.1	68.8	7.63	—	129
7.5						3.2	25.5	71.3	7.64	—	139
8.5						2.1	27.6	70.3	7.65	—	136
9.5						4.0	24.4	71.6	7.63	—	—
10.5						5.6	23.2	71.2	7.61	—	—
11.5						2.4	22.0	75.6	7.70	—	—
12.5						4.6	22.8	72.6	7.64	—	—
13.5						4.1	27.3	68.3	7.60	—	—
14.5						5.0	19.3	75.7	7.66	—	137

Worker's Signature R S Berger Date 3-13-90

Corroborating Witness D W. Mass Date 7/28/93

32

LABORATORY BOOK NO. SI 6055

ASSIGNED TO P. J. Corrigan

TRANSFERRED TO R. S. Berger 3/26/90
DATE

CORRESPONDING LOOSE-LEAF NOTEBOOK

DATE ISSUED 11-14-89

DATE RETURNED 11-10-93

SUBJECT

BS

INSTRUCTIONS FOR ENTERING DATA IN LABORATORY NOTEBOOKS.

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B. Describe the purpose of the work, give a narrative description of what was done, and indicate the sequence in which each step was taken. Cross Reference data entries as appropriate for maximum clarity. For example, if analytical results on coded samples are entered in the notebook, enter the notebook and page number where the sample description can be found and provide references to procedures or analytical methods used.

C. Define trade-named materials, acronyms or jargon, the first time they are used. Show the mathematical formula for all calculations and a sample calculation if the principle is not obvious. Computer programs used for data analysis should be referenced.

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Date 2-14-90

Subject FG Base

Standard run using Sodium Methoxide as catalyst

146g 1395-39 Methyl Esters added to the reactor. 24g K^+ soap, 34.4g of sucrose then added. Then 2.18g of CH_3ONa soln added. Vac turned on and temp raised to 135°C. Pressure held at 15 mmHg in stage 1. After 1.5 hrs add 205g of esters + 2.26 g of CH_3ONa soln.

TIME		TEMP°C	PRESSURE mmHg	
8:05		135	15	
8:35		135	15	
9:05		135	15	
9:35	SAMPLE (1.5)	135	15	205g esters + 2.26g CH_3ONa soln added.
9:45		135	1.5	Slight Bubble over
10:15		135	3.2	
10:45	SAMPLE (2.5)	135	3.4	— Pressure jumping to 6.0 o
11:15		135	1.6	Vac problems throughout the reaction
11:45	SAMPLE (3.5)	135	1.5	
12:15		135	1.0	] pressure jumping from 0.5 to 2.0
12:45	SAMPLE (4.5)	135	0.5	
1:15		135	1.0	Vac. to 3.2mm
1:45	SAMPLE (5.5)	135	0.5	

HRS	1	2	3	4	5	6	7	8	I-BAR	SUCROSE	DFK
1.5	29.8	27.0	34.8	8.3					1.94	6.26	
2.5	1.1	3.1	10.0	19.7	19.8	21.8	17.5	7.0	4.77	—	
3.5					8.2	24.3	37.0	30.5	6.78	—	
4.5					1.9	5.6	31.6	60.9	7.45	—	153
5.5					4.2	4.7	24.9	70.3	7.61	—	179

Worker's Signature R. S. Berger Date 2-13-90

Corroborating Witness D. W. Mann Date 7/27/93

30 Date 2-15-90

Subject EG Base

Standard run using sodium methoxide

146g esters 1395-39, 24g K+ soap, 34.4g sucrose + 1.3 g sodium methoxide. Stage 1 pressure at 15 mmHg. Stage 2 add 205g esters + 1.3 g sodium methoxide.

TIME		TEMP °C	PRESSURE mmHg	
8:10		135	15	
8:40		135	15	
9:10		135	15	
9:40	SAMPLE(1.5)	135	15	205g ester + 1.3g CH_3ONa soln.
9:50		135	1.2	
10:20		135	1.5	
10:50	SAMPLE(2.5)	135	2.2	
11:20		135	3.2	
11:50	SAMPLE (3.5)	135	1.8	
12:20		135	1.2	
12:50	SAMPLE (4.5)	135	0.9	
1:20		135	0.7	
1:50	SAMPLE (5.5)	135	0.5	
2:20		135	0.5	
2:50	SAMPLE (6.5)	135	0.5	Run Ended

HRS	1	2	3	4	5	6	7	8	I-BAR	SUCROSE	DEK	
1.5	57.1	29.4	10.7	2.8					1.41	9.95		
2.5	17.8	28.1	27.2	15.6	8.4	2.8			2.36	0.93		
3.5		0.5	2.3	5.3	13.6	23.9	33.0	21.6	6.16	—		
4.5					2.1	8.5	28.8	60.6	7.40	—	118	
5.5						2.2	12.8	85.0	7.80	—	208	
6.5						2.0	11.7	86.4	7.82	—	221	

Worker's Signature R S Berger Date 2-15-90

Corroborating Witness B W. Mann Date 7/27/93

36 Date 2-26-90

Subject EG Base

Dropwise addition of stage 2 esters w/ Sodium methoxide @ 25mmHg

Stage 1: 146g 1395-39 esters, 24g K+ soap, 34.4g sucrose & 1.0g sodium methoxide. Stage 1 pressure at 15 mmHg

Stage 2: Add 205g of esters dropwise over 5 hrs. Add 1.0g sodium methoxide. Hold pressure at 25mmHg.

TIME		TEMP °C	PRESSURE mmHg	
8:10		135	15	
8:40		135	15	
9:10		135	15	
9:40	SAMPLE (1.5)	135	15	1.0g CH_3ONa solution added - 205g ester dropwise
10:10		135	15	
10:40	SAMPLE (2.5)	135	15	
11:10		135	15	
11:40	SAMPLE (3.5)	135	15	
12:10		135	15	
12:40	SAMPLE (4.5)	135	15	
1:10		135	15	
1:40	SAMPLE (5.5)	135	15	
2:10		135	15	
2:40	SAMPLE (6.5)	135	15	
3:10		135	15	Esters all in at 3:20
3:40	SAMPLE (7.5)	135	15	Nitrogen on overnight
8:00	2/27	135	15	Reaction restarted
8:30		135	15	
9:00	SAMPLE (8.5)	135	15	
9:30		135	15	
10:00	SAMPLE (9.5)	135	15	
10:30		135	15	
11:00	SAMPLE (10.5)	135	15	

Worker's Signature R. S. Burger Date 2-26-90

Corroborating Witness D. W. Mann Date 7/28/93

Date 2-27-90

Subject F6 Base

cont. from last page

TIME		TEMP'C	PRESSURE mmHg	
11:30		135	15	
12:00	SAMPLE (11.5)	135	15	
12:30		135	15	12:25 1.0g sodium methoxide added
1:00	SAMPLE (12.5)	135	15	
1:30		135	15	
2:00	SAMPLE (13.5)	135	15	
2:30		135	15	
3:00	SAMPLE (14.5)	135	15	Run Ended

HRS	1	2	3	4	5	6	7	8	I-BAR	SUCROSE	DEX	%ME
1.5	51.9	32.4	12.6	3.1					1.48	8.07		64.2
2.5	25.7	30.5	27.6	12.3	3.3	0.5			2.05	0.97		55.1
3.5	5.4	15.5	23.8	27.5	16.8	9.1	1.9		3.26	0.13		52.4
4.5	0.8	4.2	13.1	22.5	23.7	19.8	11.8	4.1	4.48			38.4
5.5			11.8	15.0	21.5	25.9	19.4	6.4	5.12			38.9
6.5			2.0	6.2	15.8	26.5	32.7	16.9	6.10			51.1
7.5			1.1	4.4	12.3	25.9	35.1	21.3	6.34			44.8
8.5				1.3	7.1	21.3	36.2	34.0	6.81			44.5
9.5					2.9	18.5	43.5	35.0	7.02			44.9
10.5					0.8	20.1	44.0	35.1	7.06			44.7
11.5					0.8	16.5	46.6	36.2	7.11			44.0
12.5					1.3	11.8	37.0	49.9	7.28			45.0
13.5						6.8	26.7	66.5	7.55		155	39.7
14.5						3.2	22.9	73.8	7.67		150	39.8

Worker's Signature R S Berger Date 2-27-90

Corroborating Witness B W. Mann Date 7/28/93

38 Date 2-28-90

Subject F6 Base

½ soap + sodium methoxide

146g 1395-39 esters, 12g K⁺ soap, 34.4g sucrose + 1.0g sodium methoxide in stage 1 at 15mmHg. 205g esters and 1.0 g sodium methoxide added to stage 2.

TIME		TEMP°C	PRESSURE mmHg	
8:05		135	15	
8:35		135	15	
9:05		135	15	
9:35	SAMPLE (1.5)	135	15	205g ester + 1.0 g sodium methoxide
9:45		135	1.3	
10:15		135	2.0	
10:45	SAMPLE (2.5)	135	2.7	
11:15		135	3.8	
11:45	SAMPLE (3.5)	135	4.0	
12:15		135	3.9	Vac. Problems
12:45	SAMPLE (4.5)	135	3.8	
1:15		135	3.6	
1:45	SAMPLE (5.5)	135	3.9	Reaction Stopped
~~2:15~~		~~135~~	~~4.0~~	
~~2:45~~	~~SAMPLE (6.5)~~	~~135~~	~~4.0~~	

HRS	1	2	3	4	5	6	7	8	IVBAR	SUCROSE	DFK
1.5	55.8	33.2	10.9						1.41	10.39	
2.5	12.1	20.9	22.2	17.3	13.7	13.8			2.84	1.30	ND
3.5			1.6	6.3	14.3	25.2	32.8	19.7	6.17	—	DFK's
4.5			0.3	2.0	6.7	17.7	35.7	37.8	6.84	—	Submitted
5.5					1.7	9.0	33.4	55.9	7.36	—	

Worker's Signature Q L Berger Date 2-28-90

Corroborating Witness B D W. Mann Date 7/28/93

86 Date 5-29-90

Subject FG Base

.025% moles $KOCH_3$ / mole sucrose

Add 146g 1395-39 Methyl Esters to the reactor. Then add 2.4g K^+ soap, 34.4g sucrose + 0.7g $KOCH_3$. Raise temp to 135°C + vac at 15mmHg for stage 1. After 1.5hrs add 20.5g esters + 0.7g $KOCH_3$ and vac > 0.5mmHg

TIME		TEMP°C	PRESSURE mmHg	
8:30		135	15	
9:00		135	15	
9:30		135	15	
10:00	SAMPLE (1.5)	135	15	20.5g esters + 0.7g $KOCH_3$
10:05		135	3.1	
10:35		135	1.9	
11:05	SAMPLE (2.5)	135	2.7	
11:35		135	3.2	
12:05	SAMPLE (3.5)	135	2.9	
12:35		135	1.9	Vac. problems throughout the reaction.
1:05	SAMPLE (4.5)	135	1.2	
1:35		135	2.0	
2:05	SAMPLE (5.5)	135	2.5	← RUN ENDED
2:35				
3:05	SAMPLE (6.5)			

HRS	1	2	3	4	5	6	7	8	I-BAR SUCROSE	DFK	
1.5	44.6	33.2	22.2						1.58	8.45	
2.5	22.9	37.8	32.9	6.3					2.00	0.78	
3.5				9.7	14.7	26.2	30.7	18.7	6.12	0.16	
4.5						5.0	29.7	65.3	7.56	—	
5.5						3.3	14.7	82.0	7.75	—	164

Worker's Signature R S Berger Date 5-29-90

Corroborating Witness D W. Mann Date 7/29/93

Date 5-30-90

Subject FG Base

.025 moles $KOCH_3$/mole sucrose

Stage 1: 146g esters 1395-39, 24g K+ soap, 34.4g sucrose (fondant) + 0.7g $KOCH_3$.
Raise temp to 135°C & pressure at 15 mm Hg.

Stage 2: Add 205g esters + 0.7g $KOCH_3$.

TIME		TEMP°C	PRESSURE mmHg	
7:55		135	15	
8:25		135	15	
8:55		135	15	
9:25	SAMPLE (1.5)	135	15	205g esters + 0.7g $KOCH_3$
9:30		135	1.3	
10:00		135	2.5	
10:30	SAMPLE (2.5)	135	3.2	
11:00		135	2.9	
11:30	SAMPLE (3.5)	135	1.7	
12:00		135	0.6	
12:30	SAMPLE (4.5)	135	0.5	
1:00		135	0.6	
1:30	SAMPLE (5.5)	135	0.5	
2:00		135	0.5	
2:30	SAMPLE (6.5)	135	0.5	Run Ended

HRS	1	2	3	4	5	6	7	8	I-BAR	SUCROSE	DFK
1.5	43.3	38.3	18.4						4.57	1.57	
2.5	6.4	29.7	30.3	24.3	9.3				2.71	0.22	
3.5				4.6	6.5	8.9	34.3	45.8	6.92	—	
4.5						7.6	15.2	77.2	7.65	—	422
5.5						2.7	15.9	81.4	7.75	—	709
6.5						4.1	11.1	84.7	7.77	—	768

Worker's Signature R S Berges Date 5-30-90

Corroborating Witness R W. Mase Date 7/29/93

88 Date 5-31-90

Subject FG Base

0.5 mole% $KOCH_3$ / mole sucrose

146g 1395-39 Methyl Esters, 24g K^+ soap, 34.4g sucrose (fondant) + 1.4g $KOCH_3$ were added to the reactor. The temp was raised to 135°C + the vac. held at 15mmHg for stage 1. After 1.5 hrs 205g ester + 1.4g $KOCH_3$ were added.

TIME		TEMP°C	PRESSURE mmHg	
8:00		135	15	
8:30		135	15	
9:00		135	15	
9:30	SAMPLE (1.5)	135	15	205g ester + 1.4g $KOCH_3$
9:35		135	2.0	
10:05		135	4.5	
10:35	SAMPLE (2.5)	135	3.0	
11:05		135	1.0	
11:35	SAMPLE (3.5)	135	0.7	
12:05		135	0.5	
12:35	SAMPLE (4.5)	135	0.6	
1:05		135	0.5	
1:35	SAMPLE (5.5)	135	0.5	
2:05		135	0.5	
2:35	SAMPLE (6.5)	135	0.5	Run Ended

HRS	1	2	3	4	5	6	7	8	T-BAR	SUCROSE	
1.5	46.7	33.3	17.9	2.1					1.56	4.60	
2.5				5.5	18.9	18.6	23.8	33.3	6.38	—	
3.5						10.3	23.9	65.8	7.49	—	
4.5						6.2	12.0	81.8	7.71	—	764
5.5						5.1	9.9	85.0	7.76	—	688
6.5						3.7	9.3	87.0	7.80	—	804

Worker's Signature R L Berger Date 5-31-90

Corroborating Witness D W. Mace Date 7/29/93

(33)

LABORATORY BOOK NO. SI 6055

ASSIGNED TO P. J. Correjan

TRANSFERRED TO R. S. Berger 3/26/90
DATE

CORRESPONDING LOOSE-LEAF NOTEBOOK

DATE ISSUED 11-14-89

DATE RETURNED 11-10-93

SUBJECT

BS

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Date 3-26-90

Subject FG Base

Stage 2 temp at 110°C with N_2 sparge at 30 mm Hg

Run stage 1 at standard conditions: 146g 1395-39 ester, 24g Kt soap, 34.4g fondant sucrose + 1.4g K_2CO_3. React at 135°C + 15 mm Hg.

Stage 2: Add 205g esters + 1.4g K_2CO_3 React at 110°C + 30 mm Hg with N_2 sparge. Stirrer setting 5 (~600 rpm)

TIME		TEMP°C	PRESSURE mm Hg	
8:00		135	15	
8:30		135	15	
9:00		135	15	
9:30	SAMPLE (1.5)	135	15	205g ester + 1.4g K_2CO_3
9:32		110	30	
10:02		110	30	
10:32	SAMPLE (2.5)	110	30	
11:02		110	30	
11:32	SAMPLE (3.5)	110	30	
12:02		110	30	
12:32	SAMPLE (4.5)	110	30	
1:02		110	30	
1:32	SAMPLE (5.5)	110	30	
2:02		110	30	
2:32	SAMPLE (6.5)	110	30	
3:02		110	30	
3:32	SAMPLE (7.5)	110	30	Reaction stopped → cooled → N_2 on overnight.
7:50	3/27	110	30	Restarted
8:20		110	30	
8:50	SAMPLE (8.5)	110	30	
9:20		110	30	
9:50	SAMPLE (9.5)	110	30	
10:20		110	30	
10:50	SAMPLE (10.5)	110	30	

CONT. ON NEXT PAGE

Worker's Signature R S Berger Date 3-26-90

Corroborating Witness R W. Mason Date 2/28/93

56 Date 3-27-90

Subject F6 Base

30mm +N_2 at 110°C in stage 2

CONT. FROM LAST PAGE

TIME		TEMP°C	PRESSURE mmHg	
11:20		~~135~~ FB 110	30	
11:50	SAMPLE (11.5)	~~135~~ FB 110	30	
12:20		~~135~~ FB 110	30	
12:50	SAMPLE (12.5)	~~135~~ FB 110	30	
1:20		110	30	
1:50	SAMPLE (13.5)	110	30	
2:20		110	30	
2:50	SAMPLE (14.5)	110	30	Run Ended

HRS	1	2	3	4	5	6	7	8	I-BAR	SUCROSE	DEK	MeOH (ppm)
1.5	11.6	28.6	23.9	35.9					2.53	1.25		
2.5	3.7	14.6	26.0	24.9	15.6	15.2			3.38	0.22		61.3
3.5	1.3	4.7	14.9	21.6	18.5	16.8	19.1	3.1	4.44	0.13		33.3
4.5			4.8	12.1	17.2	~~27.0~~ 25.0 RS	~~13.9~~ 27.0 CB	~~5.68~~ 13.9 FB	5.68	—		45.5
5.5				2.9	12.5	23.4	34.9	26.3	6.52	—		23.8
6.5				3.0	9.7	19.3	34.2	33.7	6.69	—		8.6
7.5					5.3	14.7	31.3	48.8	7.13	—		
8.5						10.7	21.5	67.8	7.51	—		12.6
9.5						5.9	21.3	72.8	7.62	—	90	11.7
10.5						4.2	14.9	81.0	7.73	—	128	19.9
11.5						2.2	10.1	87.8	7.83	—	157	16.1
12.5						2.2	8.9	88.9	7.84	—	174	8.7
13.5						1.6	12.5	86.0	7.82	—	227	11.4
14.5						5.4	5.3	89.3	7.80	—	201	2.6

Worker's Signature R. S. Berger Date 3-27-90

Corroborating Witness D. W. Mann Date 7/28/93

(34)

LABORATORY BOOK NO. SI 6055

ASSIGNED TO P. J. Corrigan

TRANSFERRED TO R. S. Berger 3/26/90
DATE

CORRESPONDING LOOSE-LEAF NOTEBOOK _____

DATE ISSUED 11-14-89

DATE RETURNED 11-10-93

SUBJECT _____

BS

INSTRUCTIONS FOR ENTERING DATA IN LABORATORY NOTEBOOKS.

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84 Date 5-16-90

Subject FG Base

9:1 ester / sucrose powd sucrose + powd K_2CO_3

Add 146g 1395-39 Methyl Esters to the reactor. Then add 24g K^+ soap, 34.4g powd fond. sucrose + 1.4g powd. K_2CO_3. Raise temp to 135°C + hold rxn at 15mmHg + begin the reaction. After 1.5 hrs add 164g ester + 1.4g K_2CO_3. Sparge with N_2 at 20

TIME		TEMP°C	PRESSURE mmHg	
7:50		135	15	
8:20		135	15	
8:50		135	15	
9:20	SAMPLE (1.5)	135	15	164g ester + 1.4g K_2CO_3, N_2 on
9:30		135	4.0	
10:00		135	3.5	
10:30	SAMPLE (2.5)	135	2.2	
11:00		135	1.9	
11:30	SAMPLE (3.5)	135	1.8	
12:00		135	1.8	
12:30	SAMPLE (4.5)	135	2.0	
1:00		135	2.0	
1:30	SAMPLE (5.5)	135	2.0	
2:00		135	1.9	
2:30	SAMPLE (6.5)	135	1.9	

HRS	1	2	3	4	5	6	7	8	Σ-BAR Sucrose	
1.5	23.7	28.3	26.0	18.3	3.7				2.14	1.38
2.5					2.8	15.2	35.5	46.5	7.17	—
3.5						4.7	19.3	76.0	7.67	—
4.5						3.1	11.0	85.9	7.80	—
5.5						2.4	9.8	87.8	7.83	—
6.5						3.2	8.6	88.2	7.82	—

Worker's Signature R S Berger Date 5-16-90

Corroborating Witness D W. Mann Date 7/29/93

Date 5-17-90

Subject FG Base

9:1 ester/sucrose gran. sucrose + gran. K_2CO_3

Add 146g 1395-39 Methyl Esters to the reactor. Then add 24g K^+ soap, 34.4g gran. sucrose + 1.4g gran. K_2CO_3. Raise temp. to 135°C + hold vac at 15mm Hg for stage 1. After 1.5 hrs add 164g ester + 1.4g gran. K_2CO_3. Sparge with N_2 at 20

TIME		TEMP°C	PRESSURE mmHg	
7:55		135	15	
8:25		135	15	
8:55		135	15	
9:25	SAMPLE (1.5)	135	15	164g ester + 1.4g K_2CO_3 N_2 on
9:30		135	2.3	
10:00		135	3.3	
10:30	SAMPLE (2.5)	135	4.5	
11:00		135	2.6	
11:30	SAMPLE (3.5)	135	2.2	
12:00		135	1.9	
12:30	SAMPLE (4.5)	135	1.5	
1:00		135	1.6	
1:30	SAMPLE (5.5)	135	1.5	
2:00		135	1.5	
2:30	SAMPLE (6.5)	135	1.5	

HRS	1	2	3	4	5	6	7	8	I-BAR	Sucrose
1.5	48.0	31.5	11.3	9.2					1.57	8.15
2.5		1.6	10.9	24.3	36.4	14.0	7.8	5.0	4.66	0.21
3.5						8.2	27.4	64.4	7.51	—
4.5						3.8	16.8	79.4	7.72	0.88
5.5						2.2	14.5	83.2	7.78	0.90
6.5						3.6	10.7	85.7	7.79	0.50

Worker's Signature R L Berger Date 5-17-90

Corroborating Witness B W. Mase Date 7/29/93

(35)

LABORATORY BOOK NO. ST 1373 CORRESPONDING LOOSE-LEAF NOTEBOOK _____ DATE ISSUED 10-27-88

ASSIGNED TO E.A. Kelley DATE RETURNED _____

TRANSFERRED TO _____ DATE SUBJECT _____

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54 Date 3-15-89

Subject FG Base

Reason: To Test the use of 25g K^+ soap = M.E. P8081S, No catalyst

Add 25g H_2O, 25g sucrose, 25g K^+ soap and 320g M.E. P8081S. Raise Temp. to 60°C to Evap. H_2O Raise Temp. to 135°C and start the reaction

Time	Temp °C	pressure mm Hg	Comments
9:55	135	0.8	
10:10	135	0.5	Reaction is beginning to clear
10:25	135	0.5	
10:40	135	0.6	
10:55	135	0.6	
11:10	135	0.6	
11:25 sampled	135	0.6	Reaction is allmost clear.
11:55	135	0.8	
12:25 sampled	135	1.4	Reaction is clear
12:55	135	2.0	Cloudy
1:25 sampled	135	1.5	
1:55	135	0.9	
2:25 sampled	135	0.3	
2:55	135	0.25	
3:25 ENDED	135	0.15	

R = 1.6

Y = 10

HRS	1	2	3	4	5	6	7	8	I-Bun
1.5	48.9	34.4	13.3	3.4					1.52
2.5	14.0	26.3	27.3	16.9	8.8	4.6	2.0		2.56
3.5			1.4	4.8	12.2	26.0	36.9	18.8	6.23
4.5						1.8	8.9	89.3	7.85
5.5						1.2	4.2	94.6	7.92

Worker's Signature E. J. Kelly Date 3-15-89

Corroborating Witness Date

Date 3-23-89

Subject FG Base

Reason: To Test reaction using less Soap, & No catalyst Add 25g H_2O, 25g sucrose, 12.5g K^+ Soap and 320g Methyl Ester. Raise temp. to 60°C, evaporate H_2O, raise Temp. to 135°C and start the reaction

Time	Temp. °C	pressure mm Hg	Comments:
9:20	135	0.7	
9:35	135	0.6	
9:50	135	0.5	
10:05	135	0.5	
10:20	135	0.5	
10.35	135	0.5	
10:50 sampled	135	0.7	
11:20	135	0.8	
11:50 sampled	135	1.0	
12:20	135	1.1	
12:50 sampled	135	0.9	Reaction is Clear
1:20	135	1.0	
1:50 sampled	135	1.2	
2:20	135	0.8	
2:50 sampled	135	0.35	
3:20 ended	135	0.15	

R = 0.4 Y = 1.2

HOS	1	2	3	4	5	6	7	8	I-Bo
1.5	38.9	36.0	17.8	6.0	1.2				1.70
2.5	18.6	27.2	24.0	16.2	10.1	5.0			2.39
3.5	4.6	12.9	20.7	21.8	20.7	14.8	11.0	0.4	3.56
4.5		0.3	1.6	5.4	14.1	27.8	35.5	15.2	6.13
5.5						1.0	8.8	90.2	7.87
5.75									

Worker's Signature K L Kelly Date 3-23-89

Corroborating Witness Date

58 Date 3-29-89

Subject FG Base

Reason: To Test Reaction using less Soap & NO catalyst

Add 25g H_2O, 25g sucrose, 3.13g Soap & 320g MY. Raise Temp. to 60°C. to evap H_2O. Raise Temp. to 135°C & start stage-reaction

Time	Temp °C	pressure mm Hg	Comments
9:40	135	0.5	
9:55	135	0.4	
10:10	135	0.4	
10:25	135	0.35	
10:40	135	0.35	
10:55	135	0.35	
11:10 sampled	135	0.35	
11:40	135	0.4	
12:10 sampled	135	0.45	
12:40	135	0.5	
1:10 sampled	135	0.6	
1:40	135	0.6	
2:10 sampled	135	0.6	
2:40	135	0.7	
3:10 sampled	135	0.9	
3:40	135	1.0	shut down
8:45 AM 4/4	135	0.8	
9:15 AM 4/4	135 sampled	0.8	
9:45	135	0.7	
10:15 sampled	135	0.7	Clear
10:45	135	0.7	
11:15 sampled	135	0.7	
11:45	135	0.7	
12:15 sampled	135	0.7	
12:45	135	0.5	Cloudy

Worker's Signature L L Kelly Date 3-29-89

Corroborating Witness Date

Date 4-4-89

Subject FG Base Continue from page 58

Time	Temp °C	pressure mm Hg	Comments
1:15 Sampled	135	0.4	
1:45 Sampled	135	0.35	Shut down
8:30 4/5 AM	135	0.35	
9:00 Sampled	135	0.25	
9:30	135	0.20	
10:00 ENDED	135	0.15	M.E. are Refluxing

R = 1.2 y = 3.5

HRS	1	2	3	4	5	6	7	8	I-Bar
1.5	40.4	30.9	19.3	9.3					1.71
2.5	22.8	29.0	21.2	16.6	10.4				2.21
3.5	10.1	18.1	21.0	22.0	19.3	8.6	0.8		2.99
4.5	4.9	11.7	17.8	22.5	24.6	15.6	2.9		3.58
5.5	2.9	7.9	14.5	21.6	27.0	20.0	6.1		4.00
6.5	1.1	5.0	11.9	20.8	28.3	23.8	9.0		4.46
7.5	0.7	3.5	10.5	21.1	29.8	24.3	9.7	0.3	4.55
8.5		0.7	3.7	11.4	25.0	32.9	25.7	0.5	5.42
9.5			0.8	3.7	11.9	27.3	39.2	17.0	6.34
10.5				0.2	3.3	15.9	40.4	40.2	7.08
11:00					1.7	9.3	36.8	52.2	7.32
11.5					0.5	5.6	33.1	60.7	7.49
12.5						4.9	30.5	64.6	7.55

Worker's Signature L. F. Kelly Date 4-5-89

Corroborating Witness Date

(36)

LABORATORY BOOK NO. ST 1373 CORRESPONDING LOOSE-LEAF NOTEBOOK _____ DATE ISSUED 10-27-88

ASSIGNED TO E.B. Kelley DATE RETURNED _____

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Date 5-9-89

Subject FG Base

Reason: Verifing Points on the experimental design Curve

Add 25g H_2O 25g Sucrose 0.25g K_2CO_3 11g K^+ Soap & 320g M.E. y°. Raise Temp. to 60°C to evap. H_2O. Raise Temp. to 135°C and start the reaction.

Time	Temp °C	pressure mm Hg	Comments
12:00	135	0.7	Excessive
12:15	135	0.6	foaming
12:30	135	0.7	
12:45	135	0.7	
1:00	135	0.8	
1:15	135	1.2	
1:30 Sampled	135	1.3	
2:00	135	1.7	clear
2:30 Sampled	135	2.8	cloudy
3:00	135	0.6	
3:30 Sampled	135	0.3	
3:45 ENDED	135	0.2	

R = 0.5, y = 2.1

HRS	1	2	3	4	5	6	7	8	I-Bar
1.5	23.0	29.3	22.5	13.5	8.7	3.1			2.21
2.5		0.3	2.9	7.8	15.7	26.4	32.9	41.0	5.93
3.5						1.6	1.6	96.8	7.94
3.75						1.2	0	98.8	7.96

Worker's Signature E. L. Kelly Date 5-9-89

Corroborating Witness Date

80 Date 5-10-89

Subject FG Bar

Reason: Verfing optmal point: on the experimental design Curve

Add 25g H_2O, 25g sucrose, 0.25g K_2CO_3, 8.0g K^+ soap 0.320g, M.E. ℘. Raise ~~Temp~~ to 60°C to evap. H_2O. Raise temp to 135°C and start the reaction.

Time	Temp °C	Pressure mm Hg	Comments
10:00	135	0.8	~~Pressure~~
10:15	135	0.7	~~Foaming~~
10:30	135	0.7	
10:45	135	0.8	
11:00	135	0.9	
11:15	135	1.3	
11:30 sampled	135	1.4	
12:00	135	1.8	
12:30 sampled	135	2.7	
1:00	135	0.8	
1:30 sampled	135	0.25	
1:45 ENDED	135	0.2	

R = 0.3 , y = 1.0

HRS	1	2	3	4	5	6	7	8	IBar
1.5	14.3	23.2	23.0	17.9	14.0	6.9	0.6		2.66
2.5			0.6	2.7	8.9	23.3	39.5	25.1	6.58
3.5						1.9	0	98.1	7.95
3.75						2.3	0	97.7	7.94

Worker's Signature E L Kelly Date 5-10-89

Corroborating Witness Date

Date 5-11-89

Subject FG Base

Reason; verfing optimal points on the experimental design curve
Add 25g H_2O, 25g Sucrose, 0.25g K_2CO_3, 10.0g K^+ soap a 32% m.e. y'. Raise temp. to 60°C to evap. H_2O. Raise Temp. to 135°C and start the reaction

Time	Temp °C	pressure mm Hg	Comments
9:20	135	0.8	Excessive
9:35	135	0.5	foaming
9:50	135	0.6	)
10:05	135	0.6	
10:20	135	0.8	
10:35	135	1.0	
10:50 sampled	135	1.2	
11:20	135	1.8	
11:50 sampled	135	2.7	
12:20	135	1.2	
12:50 sampled	135	0.4	
1:05 ENDED	135	0.2	

R = 0.2, y = 1.1

HRS	1	2	3	4	5	6	7	8	I-Bar
1.5	20.7	28.3	23.1	14.7	9.7	3.5			2.30
2.5	0.4	2.4	8.7	15.6	21.6	26.3	21.2	3.8	5.00
3.5						2.7	2.7	94.5	7.90
3.75						2.0	1.0	97.0	7.93

Worker's Signature R. L. Kelly Date 5-11-89

Corroborating Witness Date

(37)

LABORATORY BOOK NO. ST 1373 CORRESPONDING LOOSE-LEAF NOTEBOOK _____ DATE ISSUED 10-27-88

ASSIGNED TO E.K. Kelley DATE RETURNED _____

TRANSFERRED TO _____ DATE SUBJECT _____

_____

_____

INSTRUCTIONS FOR ENTERING DATA IN LABORATORY NOTEBOOKS.

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B. Describe the purpose of the work, give a narrative description of what was done, and indicate the sequence in which each step was taken. Cross Reference data entries as appropriate for maximum clarity. For example, if analytical results on coded samples are entered in the notebook, enter the notebook and page number where the sample description can be found and provide references to procedures or analytical methods used.

C. Define trade-named materials, acronyms or jargon, the first time they are used. Show the mathematical formula for all calculations and a sample calculation if the principle is not obvious. Computer programs used for data analysis should be referenced.

D. Enter factual results only. These include data as well as observations. Opinions should not be recorded in the notebook. Comments implying failure should be avoided.

E. Make entries on a given subject on consecutive pages where practical. Restrict each page to a single subject or test. When considerable work on a single subject is to be done, reserve a single notebook for the work whenever practical.

F. Do not skip pages. When unavoidable, cross through blank page(s) in ink, initial and date. Blank partial pages should also be crossed through in ink, initialed and dated.

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H. DO NOT USE HIGHLIGHTER.

ATTACHMENTS

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C. FOLD-OUT ATTACHMENTS AND OVERLAPPING ATTACHMENTS ARE STRICTLY PROHIBITED.

SIGNATURES AND DATES

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RESPONSIBILITY

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86 Date 5-23-89

Subject FG Base

Reason: Trying to reduce DFK by lowing temp. after low SE AV

Add 15gm H_2O 25g sucrose, 0.25g K_2CO_3 9g K^{tt} soap & 320g formed M.E.O.; Raise Temp. to 60°C to evap. H_2O. Raise Temp to 135°C and start the reaction.

Time	Temp °C	pressure mm Hg	Comments
9:30	135	0.9	
9:45	135	0.5	
10:00	135	0.6	
10:15	135	0.7	
10:30	135	0.9	
10:45	135	0.9	
11:00 sampled	135	1.0	
11:30	135	1.7	
11:45 sampled	135	2.0	
12:00	100	0.5	
12:30	100	0.5	
1:00 sampled	100	0.5	
1:30	100	0.6	
2:00 sampled	100	0.4	
2:30	100	0.4	
3:00 sampled	100	0.5	
3:30	100	0.5	
4:00 sampled	100	0.6	
8:10 5/24	100	0.6	
8:40	100	0.5	
9:10 sampled	100	0.6	
9:40	100	1.2	vaccum leak
10:10 sampled	100	0.4	
10:40	100	0.35	
11:20 sampled	100	0.3	

Worker's Signature K. L. Kelly Date 5-23-89

Corroborating Witness Date

Date 5-24-89

Subject EG Base Continued from Page 86

Time	Temp °C	pressure
11:40	100	0.3
12:10 Sampled	100	0.2
12:40	100	0.2
1:10 Sampled	100	0.2
1:40	100	0.2
2:10 Sampled	100	0.2

R = 0.3, y = 1.1

	HRS	1	2	3	4	5	6	7	8	I-Bar
	1.5	24.9	32.8	23.3	10.4	6.6				2.08
	2.25	4.1	13.9	22.9	23.9	22.4	12.8			3.42
	3.5	1.0	5.5	14.4	21.1	24.5	22.4	8.0	3.1	4.35
	4.5	0.2	1.1	8.1	16.2	23.4	28.5	20.3	2.3	5.08
	5.5		0.6	4.8	10.8	19.0	28.4	27.9	8.4	5.58
	6.5		0.2	2.3	6.4	14.1	26.8	35.2	15.0	6.07
	7.5				1.0	5.8	18.7	39.3	35.3	6.90
	8.5					2.2	8.8	24.9	64.2	7.43
	9.5					0.7	5.6	13.1	80.7	7.69
151	10.5						3.7	7.4	88.9	7.82
	11.5						3.3	3.3	93.5	7.88
220	12.5						2.3	2.3	95.3	7.91
217/234	13.0						3.0	3.0	94.0	7.89

Worker's Signature K L Kelly Date 5-24-89

Corroborating Witness Date

38

LABORATORY BOOK NO. ST 1373 CORRESPONDING LOOSE-LEAF NOTEBOOK _____ DATE ISSUED 10-27-88

ASSIGNED TO E.A. Kelley DATE RETURNED _____

TRANSFERRED TO _____ DATE SUBJECT _____

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Date 9-29-89

Subject FG Base

Reason; To Test 1/8 sucrose/methyl ester ratio for FG reaction
Add 100 g MEOH, 25g I-1 K soap, 25g Sucrose, 0.75g K_2CO_3
and 172.8 g SI 1374-18-3 methyl ester, evap. MEOH.
Raise Temp to 135°C and start the reaction

Time	Temp °C	pressure mmHg	Comments
8:45	135	2.0	
9:00	135	0.8	
9:15	135	0.8	
9:30	135	1.5	
9:45	135	1.5	
10:00	135	1.3	
10:15 Sampled	135	0.9	
10:45	135	0.5	
11:15 Sampled	135	0.25	
11:45	135	0.25	
12:15 Sampled	135	0.15	
12:45	135	0.15	
1:15 Sampled	135	0.10	
1:45	135	0.10	
2:15 Shutdown	135	0.10	
8:35 start up	135	0.10	10 lb
9:05	135	0.10	
9:35 sampled	135	0.05	
10:05	135	0.05	
10:35 Sampled	135	0.05	
10:05	135	0.05	
11:35 Sampled	135	Shutdown 0.05	
1:35 start up	135	0.10	
2:05	135	0.05	
2:35 sampled	135	0.05	

Worker's Signature G F Kelly Date 9-29-89

Corroborating Witness Date

Date 10-2-89

Subject F6 Base

Continues from Page 147

Time	Temp °C	pressure mmHg	Comments
3:05	135	0.05	
3:35	135	0.05	

HRS.	% Sucrose	1	2	3	4	5	6	7	8	IBar	% ME
1.5	0.24	0.2	1.2	6.1	12.9	19.4	22.4	23.6	14.2	5.44	26.6
2.5	0			1.2	3.6	10.6	21.2	33.2	30.3	6.52	7.6
3.5	0			0.6	0.8	4.7	15.1	32.4	46.3	7.03	9.2
4.5	0				0.3	2.6	12.3	29.0	55.8	7.28	7.7
5.5	0				0.2	1.8	9.8	26.9	61.3	7.39	6.4
6.5	0					0.9	7.7	25.8	65.6	7.50	6.8
7.5	0					1.4	7.2	21.3	70.1	7.54	5.4
8.5	0						5.0	20.5	74.5	7.65	4.8
9.5	0						5.2	21.2	73.6	7.64	5.1
10.5	0						5.5	20.5	74.0	7.64	4.6
Soap Removed 10.5	0						5.0	20.7	74.3	7.65	5.5

Worker's Signature E. L. Kelly Date 10-2-89

Corroborating Witness Date

Date 10-3-89

Subject FG Base

Reason: To determine How much ester is really needed to run FG

Add 100g MEOH, 25g K soap I-1, 25g Sucrose, 0.75g K_2CO_3, a 172.8, SI 1374-18-3 Methyl ester. Evap MEOH, Raise temp to 135°C to start the reaction. a little more than 1:9 sucrose: methyl ester usage (9.38/1)

Time	Temp °C	pressure mm Hg	Comments
10:45	135	2.0	
11:00	135	0.8	
11:15	135	1.0	
11:30	135	1.6	
11:45	135	1.4	
12:00	135	1.3	
12:15 sampled	135	1.2	29.5g SI=1374-18-3 Methyl Ester
12:45	135	0.45	
1:15 sampled	135	0.25	
1:45	135	0.15	
2:15 sampled	135	0.10	
2:45	135	0.10	
3:15 sampled	135	0.05	
3:45 shutdown	135	0.05	
8:00 start up	135 10/4	0.10	
8:30 sampled	135	0.05	
9:00	135	0.05	
9:30 sampled	135	0.05	
10:02	135	0.05	
10:30 Ended	135	0.05	

Worker's Signature E L Kelly Date 10-3-89

Corroborating Witness Date

150 Date 10-4-89

Subject FG Base

Reason: To Determine how much Ester is really needed to run FG react. Add 100g MEOH 25g I-J K^+ soap, 25g Sucrose, 0.75g K_2CO_3 172.8g SI 1374-18-3 Methyl Ester. Rxis. Temp to evap. MEOH, Raise Temp. to 135°C and start the reaction. (8.1/1)

Time	Temp °C	pressure mmHg	Comments
1:05	135	1.5	
1:20	135	0.8	
1:35	135	0.4	
1:50	135	1.5	
2:05	135	1.5	
2.20	135	1.0	
2:35 sampled	135	0.5	2.16g SI 1374-18-3 methyl Ester.
3:05	135	0.3	
3:35 sampled	135 shutdown	0.2	
7:55	135	0.35	
8:25	135	0.20	
9:55 sampled	135	0.15	
9:25	135	0.10	
9:55 sampled	135	0.10	
10:25	135	0.10	
10:55 sampled	135	0.05	
11:25	135	0.05	
11:55 sampled	135	0.05	
12:25	135	0.05	
12:55 sampled	135	0.05	
1:25	135	0.05	
1:55 sampled	135	0.05	
2:25	135	0.05	
2:55 sampled	135	0.05	
3:25	135	0.05	
3.55 ENDED	135	0.05	

Worker's Signature K. L. Kelly Date 10-4-89

Corroborating Witness Date

Date 10-6-89

Subject FG Base

Reason: To determine how much Ester is really needed to Run FG Reaction
Add 100g MEOH 25g I-1 K Soap, 25g sucrose 0.75g K_2CO_3 & 172.8g methyl Ester SI 1374-18-3, Evap. MEOH and raise Temp. to 135°C to start the reaction (8.2/1)

Time	Temp °C	pressure mm Hg	Comments
10:05	135	1.8	
10:20	135	0.9	
10:35	135	0.9	
10:50	135	1.6	
11:05	135	1.7	
11:20	135	1.5	
11:35 Sampled	135	0.9	Add 4.32g SI 1374-18-3 ME.
12:05	135	0.4	
12:35 Sampled	135	0.2	
1:05	135	0.2	
1:35 Sampled	135	0.15	
2:05	135	0.15	
2:35 Sampled	135	0.05	
3:05	135	0.05	
3:35 shutdown	135	0.05	
8:00 start up	135	0.10	
8:30	135	0.10	
9:00 Sampled	135	0.10	
9:30	135	0.05	
10:00 Sampled	135	0.05	
10:30	135	0.05	
11:00 Sampled	135	0.05	
11:30	135	0.05	
12:00 Sampled	135	0.05	
12:30	135	0.05	
1:00 ENDED	135	0.05	

Worker's Signature K. L. Kelly Date 10-6-89

Corroborating Witness Date

152 Date 10-5-89

Subject FG Continue from Page 149

	HRS	% Sucrose	1	2	3	4	5	6	7	8	IBar	% IE
	1.5	0.3			4.7	11.4	18.1	22.9	25.3	17.7	5.74	20.8
SI 1373-150	2.5	0.1				2.1	7.9	18.6	33.4	38.1	6.82	13.5
	3.5	0.1				0.6	2.5	12.1	28.7	56.1	7.27	9.9
	4.5						2.0	10.6	23.9	63.5	7.41	8.4
	5.5						1.2	8.3	20.1	70.4	7.53	7.5
	6.5						0.9	6.9	16.8	75.4	7.61	7.0
	7.5							6.0	14.0	80.0	7.7	6.6
	8.5							2.9	14.8	83.3	7.76	6.6
	9.5							5.4	15.2	79.4	7.70	6.4
	10.5							5.7	15.5	78.8	7.69	5.8

	HRS	% Sucrose	1	2	3	4	5	6	7	8	IBar	% IE
	1.5	0.39	1.0	2.4	6.8	13.2	19.4	22.0	22.7	12.4	5.19	24.9
SI 1373-149	2.5					0.6	5.0	13.8	27.7	52.9	7.15	20.5
	3.5						0.4	6.5	19.4	73.8	7.61	16.4
	4.5							5.8	5.8	88.3	7.79	19.3
	5.5							5.8	2.9	91.3	7.82	15.6
	6.5							4.7	2.3	93.0	7.85	15.8
	7.5							4.4	2.4	83.2	7.86	15.8

Worker's Signature E Kelly Date 10-5-89

Corroborating Witness Date

Date 10-10-89

Subject FG Base

Reason: To determine how much ester is needed to run the FG Reaction Add 100g MEOH, 25g I-1 K soap, 25g sucrose 0.75g K_2CO_3 + 172.8g SE 1374-18-3 Methyl ester. Raise Temp to evap. MEOH. Raise Temp. to 135°C and start the reaction (8.3/1)

Time	Temp °C	pressure mm Hg	Comments
9:25	135	1.1	
9:40	135	0.5	
9:55	135	0.45	
9:10	135	0.8	
9:25	135	1.2	
9:40	135	1.2	
9:55 sampled	135	0.8	6.48g SE1374-18-3 Methyl ester
10:25	135	0.5	
10:55 sampled	135	0.35	
11:25	135	0.2	
11:55 sampled	135	0.15	
12:25	135	0.10	
12:55 sampled	135	0.10	
1:25	135	0.05	
1:55 sampled	135	0.05	
2:25	135	0.05	
2:55 Sampled	135	0.05	
3:25	135	0.05	
3:55 shutdown	135	0.05	
9:00 start up	135 10/11	0.05	
9:30	135	0.05	
9:00 sampled	135	0.05	
9:30	135	0.05	
10:00 sampled	135	0.05	
10:30	135	0.05	
11:00 ENDED	135	0.05	

Worker's Signature L. L. Kelly Date 10-10-89

Corroborating Witness Date

154 Date 10-10-89

Subject FG Base

	HRS	% Sli.	1	2	3	4	5	6	7	8	I-Bar	% ME
ST 1373-151	1.5	0		0.8	4.2	11.1	19.7	25.0	25.9	13.2	5.63	23.8
	2.5	0				1.2	6.5	18.4	34.3	39.6	6.91	15.1
	3.5					0.5	3.7	12.5	27.3	55.9	7.24	11.0
	4.5						1.6	9.6	21.7	67.1	7.47	9.3
	5.5						1.6	8.8	19.7	69.9	7.51	8.1
	6.5						1.0	7.7	17.5	73.8	7.58	7.8
	7.5							5.9	15.9	78.2	7.68	7.4
	8.5							6.3	15.2	78.5	7.68	8.0
	9.5						0.6	8.7	16.7	74.0	7.58	7.0
	10.5						0.5	6.5	15.1	77.9	7.65	7.5

	HRS	% Sli	1	2	3	4	5	6	7	8	I-Bar	% ME
ST 1373-153	1.5	0.25	0.2	2.0	8.5	16.3	21.6	22.0	19.3	10.1	5.10	27.7
	2.5	0			1.3	2.8	8.8	19.8	34.0	33.4	6.63	16.5
	3.5					0.3	3.1	13.0	30.6	53.0	7.23	11.1
	4.5						1.8	10.5	24.8	62.9	7.41	9.4
	5.5						1.7	7.8	19.9	71.3	7.55	8.3
	6.5						0.3	5.6	17.7	76.4	7.65	7.6
	7.5							4.9	14.8	80.3	7.71	7.0
	8.5							4.1	12.7	83.2	7.75	6.1
	9.5							4.6	13.8	81.6	7.73	6.8
	10.5						1.1	5.8	12.7	80.4	7.67	6.2

Worker's Signature R J Kelly Date 10-10-89

Corroborating Witness Date

(39)

RESTRICTED CIRCULATION

RETENTION LIMIT: ORIGINATOR AND LIBRARY - 1/1/94
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INDUSTRIAL CHEMICALS PRODUCT DEVELOPMENT BIWEEKLY REPORT

P. J. CORRIGAN

PERIOD ENDING JANUARY 25, 1989

We are starting construction of a laboratory-scale continuous reaction system.

FG REACTION TECHNOLOGY

We are beginning construction of a laboratory-scale continuous reaction system. This system is intended to bridge the gap between the 1-liter batch reactors and the larger continuous systems. It will have four major functions.

1. Fundamental studies of the FG reaction.
2. Rapid assessment of continuous system parameter changes.
3. Sample production of unusual products.
4. Qualification of raw materials.

This system is designed to be operated by a single person, therefore, the two key design parameters are safety and ease of operation. This system will also be very flexible so that major changes can be made relatively easily and inexpensively.

The first phase of this system will be the construction and operation of a Stage 1 reactor. This reactor will have automatic level and pressure control, feed and product tanks for extended operation, and manual sampling. Once this is operating satisfactorily, one or more additional reactors will be added, along with an automatic sampling system.

This reaction system will be located in the laboratory area of C2B06. It will be cooperatively operated and maintained by Drs. J. Kao, and S. D. Pearson, and myself. Initial start-up of the Stage 1 system should be in early April.

P. J. Corrigan

P. J. Corrigan

PJC/elg/1771

40

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CHEMICALS PRODUCT DEVELOPMENT DIVISION BIWEEKLY REPORT

P. J. CORRIGAN

PERIOD ENDING JULY 26, 1989

The laboratory continuous FG reaction system has been started up. Once we determine the reactor system characteristics, we can begin collecting bench scale data on FG continuous reactions.

FG REACTION TECHNOLOGY

The laboratory continuous reaction system has been started up. In its current setup, the system consists of a single 3-liter continuous reactor that operates as a stage Ia (equivalent to R600 on the 70 lb/hr system). The system has all of the associated feed systems, automatic level, temperature, and pressure controls, and feed and product tanks necessary for a continuous reaction system.

We have been using feed from the 70 lb/hr system (P90424) in order to determine the reactor operating characteristics. So far, for similar conditions of feed, temperature, and pressure, the reactor seems to have about the same time to steady state and steady state I-bar as the 70 lb/hr system. The steady state sucrose level seems to be somewhat lower than the 70 lb/hr system. We are performing some extended replicate runs in order to determine the system operating characteristics more precisely.

A key feature of this system is its ability to be operated by one person. A trained person can perform start-up, operation, and analytical. The system has numerous safety features built-in that allow its extended operation while unattended. A preliminary safety review by SWTC Buildings and Services has resulted in approval of this concept. With this feature, a single person can run the system for days.

Once the system is fully characterized, we plan on running a series of studies of soap. These will include various levels of soap, various types of soap (soap from IMF esters as well as hardstock), and soap recycling.

Now that the stage 1a system is operating, we will also begin the design and ordering of equipment for a system expansion to three reactors (Stages Ia, Ib and 2a). This will take several months. Eventually, I plan to install an automatic sampling system, so that samples can be collected overnight, while the operator is away, as well as during the day.

P. J. Corrigan/elg
P. J. Corrigan

PJC/elg/2145

Keywords: continuous reaction, lab FG reactions

RESTRICTED CIRCULATION

RETENTION LIMIT: ORIGINATOR AND LIBRARY - 1/1/94
ALL OTHERS - READ AND OUT

INDUSTRIAL CHEMICALS PRODUCT DEVELOPMENT BIWEEKLY REPORT

P. J. CORRIGAN

PERIOD ENDING MAY 17, 1989

There are more benefits from small sucrose particle size than just good sucrose utilization. Laboratory batch reactions have shown that much less soap is needed when small particle sucrose is used.

FG REACTION TECHNOLOGY

It was not so long ago when all of our reaction systems (clinical, pilot plant, laboratory) used granular sucrose and granular carbonate. Using such large particle materials will work, but at a price. The price is overuse of many (if not all) of the other reactants. Take catalyst, for example. We have found, in laboratory reactions, that when extremely fine particle sucrose is used (via water method of addition), no carbonate is needed. The residual base in the soap is enough to catalyze the reaction.

Now we have turned our attention toward soap. Ephraim Kelly recently completed a matrix experiment to determine how much soap is needed, in a batch reaction, when very fine particle sucrose is used. Coordinating with Bob Belanger, he found that the reaction runs best at about one-third the standard level of soap. One of the most surprising results of this study is that not only is the reaction better at this level of soap, but the color is much improved also. Mr. Kelly has been able to produce high octaester material with 0.1 red and 0.4 yellow (centrifuged, bleached with 1% filtrol).

It must be cautioned that these results are valid only for batch reactions. The optimum soap levels for a continuous system will undoubtedly be different. However the laboratory continuous reaction system is nearly completed, and once it is operational, we will start looking at the effect of soap level in a continuous reactor.

P. J. Corrigan

P. J. Corrigan

PJC/elg/1985

Keywords: color, particle size, soap usage

RETENTION LIMIT: ORIGINATOR AND LIBRARY - 1/1/94
ALL OTHERS - READ AND OUT

CHEMICALS PRODUCT DEVELOPMENT DIVISION BIWEEKLY REPORT

P. J. CORRIGAN

PERIOD ENDING AUGUST 23, 1989

The laboratory continuous reaction system will be used to explore particle size effects on a continuous FG reaction. It will also be used to investigate the effects of ultrasound on the reaction.

LABORATORY CONTINUOUS REACTION SYSTEM

Although we know that small sucrose particle size leads to better sucrose utilization, we still do not really know how small is "small enough." This was an area of concern during the recent Quality of Process Review. With the laboratory CSTR, we are now in a position to start addressing this issue. The laboratory CSTR is ideally suited to look at questions like this because it mimics the larger continuous systems, but requires only small amounts of material to run; 2 kg of sucrose is enough to make feed for several days' run. This small amount of sucrose enables us to pass it through a sieve tray stack, then measure the fractions in each sieve tray. In this way we can not only determine the particle size distribution, but also to purposely alter the distribution by screening out the fractions that we don't want. Over the next several weeks we will be running reactions using sucrose with progressively lower "top ends". This week we will be looking at sucrose that has all the particles above 300 microns removed. After that, we will be looking at sucrose with 200, 100, and 50 micron top ends. This information will not only allow us to operate our laboratory system better (for future studies, such as soap reduction), but it will provide information to allow the larger systems to optimally mill their sucrose.

ULTRASOUND AND METHOD OF ADDIITON

From experiments in laboratory batch reactions, and on the laboratory continuous system, we have found that applying ultrasound during the FG reaction improves the rate of sucrose utilization and lowers the final level of sucrose. This improved sucrose utilization will often lead to higher octa ester levels than might otherwise be achieved without ultrasound. Kathy Flynn has noted that ultrasound is commonly used to form microemulsions, and that our increased sucrose utilization with ultrasound may be due to microemulsion formation.

What does this have to do with method of addition? Sucrose ester researchers were very interested in microemulsions during the 1960's. The "water method of addition" and other solvent-based methods of addition (such as methanol) were developed in order to produce microemulsions in the reaction mix. We have confirmed in the laboratory that the solvent methods of addition result in reactions with extremely good sucrose utilization and high final octaester levels. However, it may be possible to obtain the benefits of the solvent methods of addition using ultrasound instead, without all of the negative side effects of the methods of addition (extreme foaming, potential ester hydrolysis, extra equipment). Our next step is to purchase a small ultrasonic flow cell that can be installed in the recirculation line of the laboratory CSTR. If this succeeds in improving the sucrose utilization, it should not be too difficult to scale this idea up to larger systems.

P. J. Corrigan

PJC/elg/2190

P. J. Corrigan

Keywords: Lab FG reactions, method of addition, particle size, sucrose

RESTRICTED CIRCULATION

RETENTION LIMIT: ORIGINATOR AND LIBRARY - 1/1/94
ALL OTHERS - READ AND OUT

CHEMICALS PRODUCT DEVELOPMENT DIVISION BIWEEKLY REPORT

P. J. CORRIGAN

PERIOD ENDING SEPTEMBER 6, 1989

What is the best form of sucrose needed to give good sucrose utilization and high octaester level in the FG reaction? That is what we are trying to find out.

SUCROSE

Sucrose is the backbone of the FG-Base molecule. Not surprisingly, we have found that the physical form of the sucrose is very important in determining how it reacts. Last year we demonstrated, using laboratory batch reactions, that smaller particle sucrose reacts faster, with less residual sucrose. Small particle sucrose also makes the reaction more robust, and therefore more tolerant of things like process upsets, and poorer quality methyl esters. I am now exploring several more areas relating to sucrose particle size reduction, and its relation to the FG reaction.

1. We are continuing to investigate sucrose particle size effects on the FG reaction using the laboratory continuous reaction system. We are dry milling the sucrose, then sieving it to remove all particles greater than a certain value. This sucrose is then reacted in the laboratory stage 1 CSTR, and then time to steady state, and steady state sucrose and Ibar are determined.

   Our tedious experience with dry milling and sieving has led to some exploration of alternative types of milling. A review of the literature, and discussions with vendors has revealed fluid energy milling as a promising option. A fluid energy mill has no moving parts. The sucrose is fed into a cylindrical chamber along with a high speed stream of air. The particles whirl around the chamber, beating each other into finer and finer particles. By varying the flow rate of the air, you can adjust the size particle that is ejected from the chamber. Larger particles are held in by centrifugal force; smaller particles flow out with the air stream. Fluid energy mills are advertised to be able to produce particles in the 1-10 micron range for materials of about the same hardness as sucrose. They have the added advantage of producing very little heat during milling, so there is less chance of sucrose degradation. I have arranged for a small pilot test of a fluid energy mill at Sturtevant, Inc. (Boston MA) this week to see how well this mill reduces sucrose particle size.

3. Last year we showed that spray dried sucrose can produce a very fine particle, amorphous material that reacts very well. Based on this work, I have arranged a spray drying pilot test this week at Custom Processing (Trenton, NJ). This toll manufacturer has extensive spray drying experience, and a GMP production unit. If this test is successful we will be able to determine the optimum conditions for spray drying sucrose. We will also have qualified a potential toll processor for larger scale production.

4. A review of the literature has shown that sucrose manufacturers routinely make a grade of sugar called fondant sugar. This type of sugar has a particle size of 20 microns or less, and is used for candy and icing (the particle size detection limit by the teeth is 30-40 microns). Manufacturers add 3-5% starch to fondant sugars in order to prevent caking, since they are highly hygroscopic. I am in the process of contacting manufacturers to see if they can provide me a sample of fondant sugar, without starch, so I can evaluate it in a laboratory reaction.

P. J. Corrigan

P. J. Corrigan

PJC/elg/2221

Keywords: particle size, sucrose

CHEMICALS PRODUCT DEVELOPMENT DIVISION - OLESTRA PROCESS MONTHLY REPORT

P. J. CORRIGAN

FOR PERIOD ENDING 3/1/90

We have been running laboratory batch reactions to investigate the role of some process variables on DFK levels. To date, we have found two good leads.

DFK AND MASS TRANSFER

Increasing the pressure in stage 2 can significantly lower the DFK level. For example, our laboratory reaction under a "standard" set of conditions produces 1089 ppm DFK at 90% octa (all DFK's mentioned here are DFK's in the crude). This standard set of conditions includes a pressure of about 0.5-1 mm in stage 2. If this reaction is rerun using 15 mm in stage 2 (and no other changes) the DFK drops to 308 ppm at 90% octa. At 25 mm in stage 2, the DFK drops to 263 at 89% octa. We have also found that reducing the agitation has a similar effect -- reducing the agitation reduces the DFK.

We believe that by increasing the pressure or decreasing the agitation, the rate of methanol removal from the mixture is reduced, thus increasing its concentration in solution. Since the rate of sucrose ester (SE) formation is proportional to $1/[MeOH]$, and the rate of beta-keto ester (BKE) formation is proportional to $1/[MeOH]^2$, any rise in the methanol concentration will reduce the rate of BKE formation (and therefore DFK) more than that of sucrose esters. This means that mass transfer of methanol is one variable we can manipulate to reduce DFK.

DFK AND ESTER CONCENTRATION

Kathy Flynn theorized that since the rate of SE formation is proportional to [ester] while the rate of BKE formation is proportional to $[ester]^2$, keeping the ester concentration in stage 2 very low (by dropwise addition) should reduce the rate of BKE more than the rate of SE. To test this, we reran the standard reaction, except in this case we added the esters dropwise to stage 2 over a 10 hour period. This reaction achieved 90 DFK at 80% octa (compare this with the standard reaction described above). Conceptually, dropwise addition could be simulated in the continuous system by a slow continuous addition of the stage 2 esters over several reactors.

If the rate of addition is doubled (dropwise over 5 hours), the DFK is 770 at 80 octa. This DFK is lower than that for the standard reaction, but much higher than that for the 10 hour addition rate. This shows that the ester concentration in stage 2 must be kept very low to reduce DFK -- when this is the only variable you are manipulating.

What if you tried manipulating both variables at once -- both mass transfer and ester concentration. Are the effects cumulative? To test this we ran the reaction at 15 mm, and added the esters over 5 hours (the faster addition rate). This reaction achieved 75 ppm DFK at 75% octa. This shows that the effects are cumulative.

Over the next several weeks we will be running more reactions varying pressure, agitation, and ester addition rate to see what is the lowest DFK we can achieve for 75-80 octa.

P. J. Corrigan

P. J. Corrigan

PJC/elg/2464

Development Record*

Compiler P. J. Corrigan Division Chemicals Date 3/14/90

Descriptive Title A PROCESS FOR MANUFACTURING HIGHER POLYOL FATTY ACID ESTERS USING A REDUCED AMOUNT OF FATTY ACID LOWER ESTERS

From: D. J. Bruno (Signature of Director, Associate Director, or Department Head)

To: R. B. Aylor Patent Counsel

A legal opinion is requested on the patentability of the development described below believed to involve worthwhile novel subject matter:

**1. What are the advantages of this development or what does it accomplish?

Most processes for making sucrose polyesters (SPE) with high conversion to octaester, require a molar ratio of fatty acid lower ester to sucrose of at least 10:1, even though the theoretical molar ratio for conversion to octaester is 8:1. In practice, high conversion to octaester cannot usually be achieved without an excess of fatty acid lower esters.

(Continued on Attachment)

**2. How are these achieved, i.e., what is the development?

There are two key steps to this development.

1) The use of very fine particle sucrose, with all particles less than about 50 microns, preferably <10 microns, and more preferably <1 micron.
2) The use of fatty acid lower esters with:
   a) Free fatty acid less than about 0.1%, preferably <0.05% and more preferably <0.01%.
   b) Carbonyl value less than about 200 ppm, preferably <100 ppm, and more preferably <50 ppm.

**3. What are the variations in the development known or reasonably predictable without losing its primary advantages?

The fatty acid lower ester to sucrose ratio can be 8.0:1 to 10.0:1. Ratios of less than 8.0:1 can be used if octaester levels <75% are desired.

Variations in sucrose particle size distribution are allowed. Only the "top end" of the particle size distribution is really important. This is described in Part 2.

*Submit two signed copies to the Patent Counsel for the submitting division.

**Describe the development under headings 1 to 4 in enough detail to make its essentials clearly understandable. See instructions and examples or consult with Patent Division. Use additional pages if more space is needed. Append pertinent drawings, reports, data, etc.

D.R. 7988
Pat. Div. to complete

**4. What are the new features embodied in this development and new results obtained by practice thereof?

The new feature is the ability to achieve high conversion to octaester with lower amounts of excess fatty acid lower esters. The literature describes processes that use at least a 10:1 ester to sucrose ratio in order to drive the chemical reaction to higher yields of octaesters. However, if very small particle sucrose, and fatty acid lower esters with <0.1% free fatty acid and <200 ppm carbonyl are used, good octaester yields can be obtained at <10:1.

(Continued on Attachment)

5. List those contributing (a) to the initial idea and (b) to the further investigation of the development.

(a) R. G. Schafermeyer (b) P. J. Corrigan

(c) List persons in other divisions with whom this development has been discussed or who may have background or have done related work.

6. Chronology of principal events in this development (particularly the conception or discovery, the first reduction to practice and any tests resulting in sale of product or exposure outside the Company), including date, nature, persons involved.

Sept. 89 R. G. Schafermeyer suggests to P. J. Corrigan that a reduced ester to sucrose ratio of 8:1 might be used to reduce DFK production in the SPE reaction. P. J. Corrigan designs a series of experiments that show that reasonable octaester levels can be achieved using 8:1. P. J. Corrigan designs a series of experiments that show that ester to sucrose ratios between 8.0:1 and 10:1 can also be used, and will give even higher octaester yields, of up to 90+%.

7. Are future tests or commercial activity planned which could result in exposure of the development outside the Company? If so, state the nature and time anticipated.

Lower ester to sucrose ratios may be run on the 70 lb/hr pilot plant, the clinical system, and the test market system.

2486 Signature of compiler of this record P. J. Corrigan

ATTACHMENT

1. What are the advantages of this development or what does it accomplish?

   However, we have discovered a method of manufacturing SPE with high conversion to octaester with as little as a molar ratio as 8:1. At 8.0:1, an octaester conversion of about 75% can be obtained.

4. What are the new features embodied in this development and new results obtained by the practice thereof?

   There are many benefits of using lower amounts of excess fatty acid lower esters.

   1) The fatty acid lower ester removal from the SPE is greatly simplified. For example, the lower esters could be removed from the SPE by steam stripping, rather than by more expensive evaporation, or solvent extraction steps.

   2) The recycle stream of lower esters can be greatly reduced or eliminated. Not only does this simplify the process mechanically, but it reduces concern about the buildup of undesirable minor components in the recycled material.

   3) Using a reduced amount of lower esters will slow the reaction of undesirable minor components that can result from reactions of lower esters with other esters (such as DFK).

   4) Using less lower esters means that a given size or equipment will have a higher capacity for SPE than if more lower esters were used.

6. Chronology of principle events in this development, date, nature, person:

   Feb. 90 P. J. Corrigan designs a series of experiments that show that a lower ester to sucrose ratio (8:1) will produce lower DFK levels in crude SPE than a higher ratio (12:1).

   Feb. 90 S. D. Pearson and others demonstrate that using a lower ester to sucrose ratio (8.5:1) can achieve reasonable octaester levels (75%) on the 70 lb/hr continuous SPE pilot plant.

PJC/elg/2486
3/15/90

ABORATORY BOOK NO. SI 1386 CORRESPONDING LOOSE-LEAF NOTEBOOK _____ DATE ISSUED June 28, 1989

SSIGNED TO J. KAO DATE RETURNED _____

RANSFERRED TO _____ DATE SUBJECT _____

_____

_____

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DATA ENTRIES

A. Enter data into the notebook as the work is being performed. Entries should be made in black ink only. DO NOT USE PENCIL to enter data in notebook. Enter the date the work is started at the top of the page. Enter the title of the work on the top line immediately following the date.

B. Describe the purpose of the work, give a narrative description of what was done, and indicate the sequence in which each step was taken. Cross Reference data entries as appropriate for maximum clarity. For example, if analytical results on coded samples are entered in the notebook, enter the notebook and page number where the sample description can be found and provide references to procedures or analytical methods used.

C. Define trade-named materials, acronyms or jargon, the first time they are used. Show the mathematical formula for all calculations and a sample calculation if the principle is not obvious. Computer programs used for data analysis should be referenced.

D. Enter factual results only. These include data as well as observations. Opinions should not be recorded in the notebook. Comments implying failure should be avoided.

E. Make entries on a given subject on consecutive pages where practical. Restrict each page to a single subject or test. When considerable work on a single subject is to be done, reserve a single notebook for the work whenever practical.

F. Do not skip pages. When unavoidable, cross through blank page(s) in ink, initial and date. Blank partial pages should also be crossed through in ink, initialed and dated.

G. Do not erase or use correction fluid in notebooks. When corrections are necessary:
   1. Cross out the original entry such that it remains legible;
   2. Enter the correction along with an explanation as to why the correction is necessary; and
   3. Date and initial the correction.

H. DO NOT USE HIGHLIGHTER.

ATTACHMENTS

A. Limit attachments to no more than one item every other page. Use rub-on glue or tape only to make attachments. Place tape or glue on at least two entire edges of the item being attached. DO NOT STAPLE attachments in notebook.

B. Attachments must be placed BETWEEN the DOUBLE LINES on the top and bottom of a page. Sign and date the item across the point of attachment. Do not reduce attachment unless the full size original exists in a referenced loose-leaf notebook. The reduction must be completely legible.

C. FOLD-OUT ATTACHMENTS AND OVERLAPPING ATTACHMENTS ARE STRICTLY PROHIBITED.

SIGNATURES AND DATES

A. Minimum patentability standards require each notebook page to have two signatures: The person doing the work and a corroborating witness. A corroborating witness must be an unbiased non-inventor who preferably witnessed performance of the work in its entirety. The person doing the work must sign and date each notebook page.

B. Good Laboratory Practices (GLP's) require all entries on a page that are made on a date other than the date at the top of the page to show the current date and initials of the person making the entry.

C. Good Manufacturing Practices (GMP's) require production records to be signed by the person doing the work and by an independent observer. Laboratory Control records are required to be dated and signed by the person doing the work and by the person reviewing the records.

RESPONSIBILITY

A. The person to whom this book is issued is responsible for returning it to issuing Library as soon as it is no longer in active use.

B. Incomplete notebooks can be transferred to another person if both parties agree to the transfer and certify the transfer with the Files Clerk at the issuing Library.

C. This notebook must be indexed and have keywords assigned by the user before return to the Library. It must also include explicit cross-reference to all other notebooks loose-leaf and hardbound which contain related work.

40 Date 9/27/89

Subject Soph Batch Reaction Filtration Exp. #1

Time	Comments
0700	Turned all utilities & vacuum system on & began melting esters in ester tank (placed a 5 micron filter & canister in oven @ 275°F)
0800	Emptied ester tank & wiped it down - Pump 164.0 lbs of ester from 9/8/89 into ester feed take - Saved 2 five gallon buckets of ester that was in the tank
0830	Ron Worshom working on heat tracing for filtration piping.
0915	Charged R303 w/ ≃ 8,500 ml of feed mix from 590911 - Pulled vacuum to remove any air
0930	Began heating R303 & set pressure @ 15mm Hg
1000	- will call this time 0 temp. @ 275°F & press @ 15mm Hg.
1030	R303 beginning to foam
10:40	Increased agitation from 680 rpm to 750 rpm to keep foam in the reactor
11:20	Foaming stopped.
12:15	Beginning to get turbid so lowered level to ≃ 4,000 & added 4,500 ml of ester & 13g. K_2CO_3
12:30	Filtered thru 5 micron filter - Pressure went sky-high immediately & relief valve blew. - Slowed pump down to lowest speed & it worked O.K for ≃ 3 minutes - After 3 minutes at slow pump speed relief valve started dripping - Press. Line before filter reading 110psi - Don't believe it since relief @ 90psi - It took 6 minutes & 40 seconds to filter entire

Worker's Signature [signature] Date 9/27/89

Corroborating Witness [signature] Date 10/9/89

Date 9/27/89

Subject 5gph BATCH EXPERIMENT FILTRATION EXP. #1

	REACTOR INTO R304
	- 6000ML COLLECTED IN R304
	- SAMPLED BEFORE & AFTER FILTER FOR ANALYSIS. (@ TEMP OF 24°F FOAMING FROM 6M TO 11M)
1:00	R304 TEMP @ 269°F & PRESS. @ 0.9mmHg. W/ SPARGE SET @ 15 ON ROTOMETER
1:15	- TOOK 3,000 ML FROM STAGE I MAT'L FROM R304 & CHARGED R301 W/ 17.
	- ADDED 3,375 ML OF ESTOL
	- " 9.75 GR. POWDERED K_2CO_3
	- STARTED CENTRIFUGAL RECIRC PUMP & BEGAN PULLING VACUUM
	- SPARGE NOT POSSIBLE ON THIS REACTOR.
1:30	R301 @ 275 R304 @ 275
	" @ ~2mmHg (OFF MANOMETER) R304 @ 0.9mmHg.
	- GOOD FLOW FROM BOTH SAMPLE COCKS.
5:30	SHUT SYSTEM DOWN.

RESULTS:		I	% SUCROSE	% OCTA	% SOAP	% K_2CO_3 DFK
STAGE I	11:00 (1.0)	1.52	3.76	–	11.89	0.15
	12:00 (2.0) (2.25)	3.50	0.27%	–	11.33	0.23
END	12:15 (2.25)	3.98	0.10	0.6%		
BEFORE FILTRATION		4.58	0.33	1.0	7.44	0.17
AFTER	"	4.80	0.05	1.0	3.53	0.04
STAGE II	1:00 (0)	5.72	–	8.9	4.04	0.09
	2:00 (1.0)	7.90	–	91.6	4.00	0.05
	3:00 (2.0)	7.99	–	99.3	3.94	0.09
	4:00 (3.0)	7.97	–	97.8	4.43	0.08 541
	5:00 (4.0)	8.0	–	100%	4.65 TITRATION	0.09 122 SEC
					K_2CO_3 SOAP	Me SE
FILTER CAKE		4.29	.74%	–	1.37% 33.96%	42.0% 152
						18.3% (SEC)

Worker's Signature [signature] Date 9/27/89

Corroborating Witness [signature] Date 9/28/89

44 Date 10/2/89

Subject 5ppb Batch Reactions. Sparge Test & Filtration Test #3

PURPOSE: SEE PG. 39 FOR FILTRATION. THE SPARGE TEST INVOLVES USING A GAS DIFFUSION STONE TO GENERATE MANY SMALL BUBBLES OF NITROGEN INSTEAD OF A FEW LARGER BUBBLES. THIS WILL BE LOOKED AT TO HELP REMOVE THE MeOH MORE EXPEDIENTLY

REACTION MATERIALS: SEE PAGE 39

PROCEDURE: SEE PG. 39

R306 WILL BE USED TO TEST THE GAS DIFFUSION STONE FOR THE SPARGING TEST AND FOR STAGE I FOR THE CONTROL & SPARGE TEST.

R304 WILL BE USED FOR STAGE II OF THE FILTRATION TEST.

R303 WILL BE USED FOR STAGE I OF THE FILTRATION TEST UPON GOING THRU THE FOAMING STAGE AND WHILE STILL IN THE CLEAR PHASE THE STAGE II MATERIALS WILL BE ADDED TO R303 BRING IT BACK UP TO 275°F & FULL VACUUM FOR ≈ 15 MINUTES. THIS PRODUCT WILL THEN BE FILTERED ON A ONE PASS INTO R304. R303 THEN WILL BE USED TO RUN THE SPARGED STAGE II.

EXPERIMENT:

TIME	COMMENTS
6:30	R304, R306, & R303 RINSED W/ ESTER & HEATED TO 230°F
	- ON 9/29/89 304, 306, & 303 REACTORS & SUCTION LINES TO PUMP WERE WASHED W/ H_2O & DAWN LIQUID
8:00	R306 & R303 CHARGED W/ FEED SLURRY
	- 9,000 mL TO R306
	- 6,000 mL TO R303

Worker's Signature [signature] Date 10/2/89

Corroborating Witness [signature] Date 10/9/89

Date 10/2/89

Subject CONT. FROM Pg. 44

TIME	COMMENTS.
9:15	R303 AT 275°F & 15 mm Hg. AGITATOR @ 660 RPM
	R306 AT 268°F & 15 mm Hg. " " 665 RPM
9:15	R306 STARTING TO FOAM
	R303 1,000 ML LAYER OF SURFACE FOAM (5,500 ML VOLUME 6187 ESTOR 17.8 CARB.
10:10	ADDED STAGE II MAT'LS TO R303
10:25	STARTED FILTRATION THRU THE 1.0 MICRON FILTER
	- 11,200 ML IN R303
	- FILTRATION TOOK 4 MIN. 50 SECONDS
	- COLLECTED 9,300 ML IN R304
	- FILTRATION TEMP. (OUTLET SIDE OF FILTER)
	268°F - 270°F
10:35	LOWERED LEVEL OF R306 TO 4,000 & PUT.
	4,000 FROM R306 INTO R303
10:40	ADDED STAGE II MAT'LS TO R306 & R303.
	- 1 3/4 # OF K_2CO_3 EACH
	- 4,500 ML ESTOR EACH
10:45	CHANGED PROCEDURE & DECIDED TO PUT SPARGE
	SYNC IN R303 & RUN R306 AS CONTROL.
	- BEGAN PULLING FULL VACUUM & SET ALL SPARGES
	TO 15 & AGITATORS TO 665 RPM
11:00	R306 1.5 mm Hg. 263°F
	R304 1.6 mm Hg. 264°F
	R303 1.9 mm Hg 264°F
	- WILL DESIGNATE THIS AS TIME ZERO FOR
	STAGE II
11:10 TO	R303 NOT RECIRC. PROPERLY SO CONNECTED A N_2
11:30	LINE TO DRAIN VALVE & BLEW OUT PUMP
	SUCTION LINE TWICE. THIS FIXED THE PROBLEM.
	TEMP HAD DROPPED TO 265°F
12:00	306 @ 1.0 mm Hg. 272°F ; 304 @ 1.25 mm Hg. 275°F ;
	303 @ 1.30 mm Hg 272°F ; ALL FIRING TO NEAR OF REACTOR

Worker's Signature [signature] Date 10/2/89

46 Date 10/2/89

Subject Cont. From Pg. 44

TIME	COMMENTS
1:00	306 @ 0.7 mM/g. 225°F ; 304 @ 1.1 mM/g. 275°F
	303 @ 0.8 mM/g 275 °F. 1,000 ML OF FOAM ON 303
	& 306 & VERY LITTLE FOAM ON R304
2:00	R303 NOT RECIRC. VERY WELL & LOSSING TEMP.
3:30	R303 DOWN TO 247°F - STATOR IS WASTED
4:00	SHUT DOWN R303 & SAMPLED R304 & THEN SHUT
	R304 DOWN.
4:45	SHUT DOWN REACTOR R306

RESULTS!

END OF STAGE I $\bar{I}$ = 2.72 0% OCTA 0.59% SUCROSE

TIME INTO STAGE II	303 $\bar{I}$	303 OCTA	304 $\bar{I}$	304 OCTA	DFK	306 $\bar{I}$	306 OCTA	DFK
0	2.81 ‡	1.4	3.26*	0.6		2.35	—	
1.0	6.71	34.4	7.40	55.9		5.86	13.8	
2.0	7.65	76.6	7.85	98.3	139	7.72	76.8	
3.0	7.96	98.7	7.94	96.2		7.83	86.7	260
4.0	7.99	99.7	7.84	96.4		7.93?	94.1?	
5.0	—	—				7.83	86.1	

‡ BEFORE FILTERING SAMPLE SUCROSE = 0.39%

* AFTER " " " = 0.24%

R306 TIME 0 SUCROSE = 0.84%

303 - Fine sparged reaction
304 - Filtered reaction
306 - control

Worker's Signature [signature] Date 10/2/89

Corroborating Witness [signature] Date 10/7/89

ABORATORY BOOK NO. SI 1386 CORRESPONDING LOOSE-LEAF NOTEBOOK _____ DATE ISSUED June 28, 1989

SSIGNED TO J. KAO DATE RETURNED _____

RANSFERRED TO _____ DATE SUBJECT _____

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C. Define trade-named materials, acronyms or jargon, the first time they are used. Show the mathematical formula for all calculations and a sample calculation if the principle is not obvious. Computer programs used for data analysis should be referenced.

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Date 12/12/89

Subject VARIABLE STAGE II TEMP/FILTRATION EXP. #2

PURPOSE: SEE PAGE 102

MATERIALS:

SOAP/ESTER MIX MADE ON 12/11/89:

1) 150 lbs I-I SOAP PREHEATED TO 205°F IN R303 THEN TRANSFERRED TO SLURRY FEED TANK.
2) ADDED 10.5 lbs OF FLAKED KOH & REACTED FOR 3.5 hours.
3) PREPARED 12 FEED BUCKETS:
   - 1,617.4 gr. SOAP/I-I MIX
   - 2,772.8 gr BLEND Y ESTER (R91001)
4) STAGE I
   ① 2 FEED BUCKETS
   ② 1540.2 gr. TWICE GROUND SUCROSE
   ③ 37.3 gr. K_2CO_3 (POWDERED)
5) STAGE II
   ① 9018 gr. ESTER
   ② 37.3 gr K_2CO_3 (POWDERED)

PROCEDURE:

1) ADDED ALL STAGE I MATERIALS TO R303 & SET TEMP TO 225°F & 15 mm Hg.
2) HEAT BATH FOR 2 hours
3) ADD ½ STAGE II ESTER & ALL STAGE II K_2CO_3 TO R303.
4) FILTER THRU 1.0 MICRON FILTER ½ OF R303 @ 2
5) ADD REMAINDER OF ESTER TO R303 & R304
6) SET TEMP TO 300°F & 5 mm Hg.
7) MAXIMUM AGITATION & RUN.
8) 15-20 ON N_2 SPARGE ROTAMETER.

[NELSON HOLE SHOWN THAT I PROCEDURE CO: TO DESIGNATE STRING BASE T. SEE PROCEDURE

Worker's Signature [signature] Date 12/12/89

Corroborating Witness _____ Date _____

106 Date 12/12/89

Subject CONT FROM 105

EXPERIMENT:

TIME	COMMENTS
8:30	ADDED STAGE I MATLS TO R303
9:00	R303 @ 275°F & 15mmHg.
9:30	STARTING TO FOAM
10:30	STOPPED FOAMING
11:00	ADDED ½ OF STAGE II ESTERS + ALL STAGE II K_2CO_3 TO R303
	- SET PRESSURE TO 5mmHg & HEAT TEMP @ 275°F
11:15	FILTERED ½ OF R303 INTO R304
11:20	ADD REMAINDER OF STAGE II ESTERS TO R303 & R304
	- SET TEMP @ 295°F & 5mmHg.
12:00	WILL REFER TO AS TIME 0
	R-303 5.5mmHg 291 & CLIMBING
	R304 5.0mmHg 288 "
1:20	MISSED THE 1:20 SAMPLES.
1:40	R303 @ 295°F 5.5 mmHg BROWN SUGAR SPKS
	R304 @ 293°F 5.2 mmHg
2:20	R303 @ 297°F 5.5 mmHg. BLACK SUGAR SPKS
	R304 @ 298°F 5.0 mmHg
3:00	R303 @ 299°F 5.0 mmHg
	R304 @ 299°F 5.25 mmHg
4:00	R303 @ 300°F 5.5 "
	R304 @ 298°F 5.25 "
5:00	R303 300°F 5.25
	R304 298°F 5.5
6:00	R303 @ 300°F 5.25 mmHg.
	R304 @ 298°F 5.5 "
7:00	SHUT DOWN SYSTEM

Worker's Signature [signature] Date 12/14/89

Corroborating Witness _____ Date _____

RESULTS:

R303 (NON-FILTERED)

		% SOAP	% K_2CO_3	IBAR	% OCTA	% SUCROSE	DFK
END OF STAGE I W/O STK II MAT'L		9.65	.56	2.91*	—	1.69*	—
0	12:00	5.46 ~~2.32~~	.53	5.76	16.6	0.98	~~5~~
1.0	1:00	5.06 ~~2.64~~	.44	—	—	0.74	79
2.0	2:00	5.71 ~~2.69~~	.41	7.15	44.6	0.65	96
3.0	3:00	5.54 ~~2.63~~	.47	—	—	—	—
4.0	4:00	5.55 ~~2.64~~	.41	7.11	41.2	-	-
5.0	5:00	5.99 ~~2.69~~	.28	—	—	-	—
6.0	6:00	5.84	.32	7.12	40.9	-	85
7.0	7:00	583	.37	7.08	40.7	—	—

R304 (FILTERED)

		% SOAP	% K_2CO_3	IBAR	% OCTA	% SUCROSE	DFK
0	12:00	5.52	.10	5.96	19.5	0.19	-
1.0	1:00	5.16	.16	7.41	61.0	0.18	316
2.0	2:00	—	—	7.61	70.9	0.19	
3.0	3:00	5.64	.07	—	—	—	-
4.0	4:00	5.83	0	7.75	81.7	—	-
5.0	5:00	5.87	0	—	—	—	-
6.0	6:00	5.96	0	7.76	82.7	—	-
7.0	7:00	5.52	0	7.80	85.3	—	331/346

* THIS HAS STAGE II MAT'LS.

Worker's Signature _____ Date _____

Corroborating Witness _____ Date _____

Date JAN 10, 1990

Subject VARIABLE STAGE II TEMP / FILT. EXP # 4

PURPOSE: SEE PAGE 102

MATERIALS: SEE PAGE 105

PROCEDURE: SEE PAGE 105

NOTES: THIS EXPERIMENT WILL BE RUN @ 250°F IN STAGE II

EXPERIMENT:

TIME	COMMENTS
07:30	CHARGED R303 w/ STAGE I MAT'LS.
0800	R303 @ 15mm Hg & 225°F
1000	ADDED ALL STAGE II K_2CO_3 TO R303
	" ½ OF STAGE II ESTERS TO R303
	SET PRESSURE TO 5.0 mm Hg.
	" TEMP TO 250°F
10:15	FILTERED ½ OF R303 INTO R304 THRU 1.0 MICRON FILTER.
10:20	ADDED REMAINDER OF STAGE II ESTER TO R303 & R304
10:30	R303 @ 245°F & 6.0 mm Hg.
	R304 @ 237°F & 5.6 mm Hg.
10:40	R303 @ 250 °F 5.6 mm Hg
	R304 @ 250 °F 5.2 mm Hg.
	- WILL REFER TO AS STAGE II TIME 2020
11:00	R303 @ 250°F & ? mm Hg (CHANGED MANOMETER.
	R304 @ 250°F & 5.1 mm Hg.
11:40	R303 @ 251°F & 5.75 mm Hg FOAMING
	R304 @ 251°F & 5.75 mm Hg "
12:00	R303 @ 250 °F & 5.25 "
	R304 " " "
12:40	R303 @ 250°F & 6.0 mm Hg. R304 @ 250°F & 5.25 mm Hg. BOIL FOAMING

Worker's Signature [signature] Date 1/10/90

Corroborating Witness _____ Date _____

112

Date JAN 10, 1991

Subject CONT. FROM PAGE 111

TIME	COMMENTS.			
1:20	R303 @ 250°F & 5.5 mm/H.	FOAMING.		
	R304 @ 250°F & 5.25 mm/H.	"		
2:00	R303 @ 250°F 5.25 mm/H.	"		
	R304 @ 250°F 5.0 mm/H.	"		
5:00	R303 @ 250°F 5.2 "	2M LEVEL OF FOAM		
	R304 @ 250°F 5.0 "	SURFACE FOAM ONLY		
5:40	SHUT DOWN SYSTEM.			

RESULTS!

R303 (UN-FILTERED)

TIME	%SCAP	%K_2CO_3	T-BAR	%OCTA	%SUCROSE	DFK
0 10:40	11.97?	.21	2.46	—	0.82	
1.0 11:40	10.41?	.14	3.57	1.1	0.21	
2.0 12:00	6.64	.14	4.67	5.1	0.21	
1:40	6.34	.11	5.62	14.9	0.43	
2:40	6.22	.09	6.03	26.4	0.24	
3.0 3:40			6.59	30.4	0.40	63
4.0 4:40			6.78	35.0	0.28	
5.0 5:40			7.09	44.0	0.40	70/74
END OF STAGE I			1.95	0	3.20	

304 (FILTERED)

AFTER FILTR.	6.93	.18	2.06	—	0.71	
0	5.48	.10	2.35	—	0.43	
1.0	5.83	.04	3.60	0.9	-	
2.0	5.74	—	5.56	11.8	—	
3.0	5.77	—	6.75	32.6	-	36/48
4.0	5.88	—	7.12	45.3	-	
5.0	5.93	—	7.27	57.4	-	85
6.0	5.87	—	7.59	68.6	-	
7.0	6.01	—	7.77	79.3	-	165

Worker's Signature _____ Date _____

Corroborating Witness _____ Date _____

Date JAN 12, 1990

Subject VARIABLE STAGE II Temp / FILTRATION EXP. #5

PURPOSE: SEE PAGE 102

MATERIALS: SEE PAGE 105

PROCEDURE: SEE PAGE 105.

NOTE: THE STAGE II TEMP OF THIS EXPERIMENT WILL BE SET AT 325°F

EXPERIMENT:

TIME	COMMENTS
7:40	CHARGED R303 W/ STAGE I MATERIAL
7:45	ROTATOR R303 DISCHARGE LINE PLUGGED
7:50	UNPLUGGED LINE
8:10	R303 @ 275°F & 15.5 mm Hg.
10:10	ADDED STAGE II K_2CO_3 TO R303
	" ½ STAGE II ESTERS TO R303
11:35	BEGAN FILTRATION OF ½ OF R303 INTO R304 THRU 1.0 micron FILTER.
11:??	RECORDED TIME AS TIME ZERO II-0
	R304 @ 10.0 mm Hg 296 & RISING
	R303 @ 9.5 mm Hg. 300 " "
11:40	R303 @ 295°F 5.25 mm Hg & VERY THICK
	R304 @ 293°F 5.0 " " " "
12:20	R303 @ 288°F 5.0 mm Hg " "
	R304 @ 297°F 5.0 mm Hg NOT AS THICK
12:40	R303 @ 293°F 4.5 mm Hg THICK
	R304 @ 300°F 5.0 mm Hg NOT SO THICK
1:20	R303 @ 316°F 5.1 mm Hg " " " BURNING
	R304 @ 324°F 4.75 mm Hg THINNING OUT BU
3:20	R303 @ 320°F 5.0 " THICK & BURNT
	R304 @ 320°F 5.25 " THIN

Worker's Signature [signature] Date 1/12/90

Corroborating Witness _____ Date _____

Date JAN 12, 1998

Subject CONT. FROM PAGE 114

TIME	COMMENTS
4:20	R303 @ 320 & 5.0 mm H. THICK
	R304 @ 320 & 5.1 mm H. O.K.
4:30	STEAM PRESSURE WAS CUT BACK BY B.S. TO 105psi R303 & R304 DOWN TO 302°F
5:20	SHUT SYSTEMS DOWN)

RESULTS:

	% Soap	% K_2CO_3	I-BAR	% OCTA	% SUCROSE	DEX
	303 (UN-FILTERED)					
END OF START	12.31	—	1.90	—	4.28	
0 11:20	6.74	.28	3.81	1.8	0.80	
1.0 12:20	6.70	.15	6.32	18.5	0.28	
2.0 1:20	6.36	.21	6.59	24.4	0.26	
3.0 2:20	6.38	.22	6.64	26.4	0.11	
4.0 3:20	5.81	.10	6.72	28.8	0.08	
5.0 4:20	6.67	.11	6.86	32.2	0.09	
6.0 5:20	5.63	.09	6.98	35.0	—	89
	304 (FILTERED)					
AFTER FILTER	5.99	.12	2.18	0	0.73	
0	5.82	.07	3.74	2.6	0.08	
1.0	6.21	.01	6.82	34.2	0	102
2.0	6.28	—	7.51	63.9	0.09	212
3.0	6.18	—	7.66	74.8	0.09	
4.0	5.98	—	7.72	78.0	—	264
5.0	5.40	—	7.72	79.1	—	
6.0	4.48	—	7.77	79.8	—	320

Worker's Signature [signature] Date 1/12/98

Corroborating Witness _____ Date _____

LABORATORY BOOK NO. SI 1386
ASSIGNED TO J. KAO
TRANSFERRED TO _____ DATE _____

CORRESPONDING LOOSE-LEAF NOTEBOOK _____

DATE ISSUED June 28, 1989
DATE RETURNED _____
SUBJECT _____

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118 Date 4/30/90

Subject PACKED COLUMN EXPERIMENT # 1

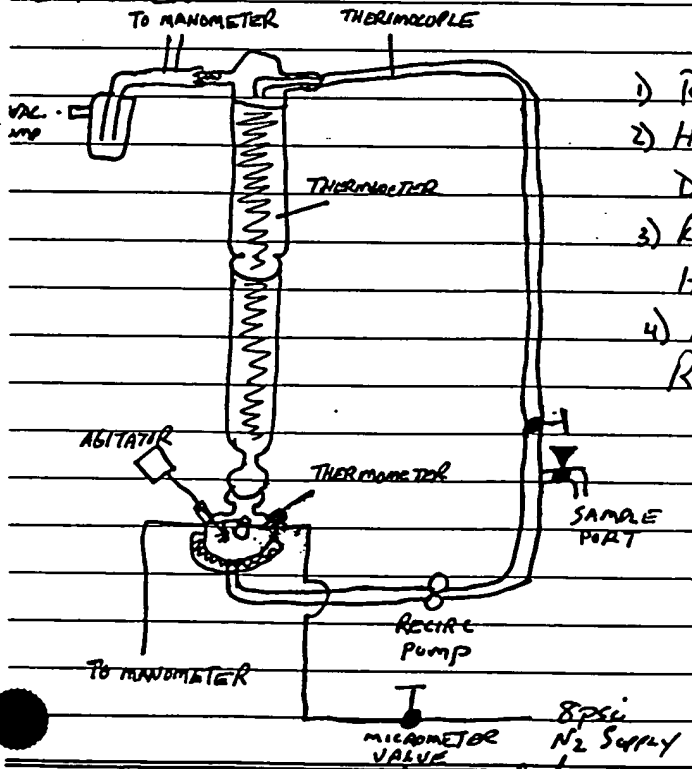
PURPOSE: TO PRODUCE 75% OCTA F.G. BY USE OF A PACKED COLUMN DURING STAGE II REACTION. BENEFITS HOPED TO ACHIEVE:

① USE OF LESS VACUUM → LOWER CAPITAL IN NATIONAL EXPANSION
② USE OF LOWER ESTER TO SUCROSE RATIOS → REDUCE OR ELIMINATE ESTER RECYCLE & POSSIBLE ELIMINATION OF THE STRIPPING OPERATION
③ USE OF LOWER TEMPS. → LESS ENERGY CONSUMPTION
④ LOWER DFK LEVELS → RESULT OF THE ABOVE THREE ITEMS

MATERIALS:

① GRANULAR CARBONATE
② TWICE GROUND SUCROSE
③ I-85 ESTER R00201
④ SOAP (K^+ STERATE)

EQUIPMENT:



1) RECIRC. LINE IS HEAT TRACED
2) HEATING MANTLE ON POT ONLY USED DURING HEAT-UP
3) AGITATOR ONLY USED DURING HEAT-UP.
4) N_2 SUPPLY PRESSURE CAN BE REGULATED FROM 0 TO 45psi

Worker's Signature [signature] Date 5/3/90

Corroborating Witness _____ Date _____

Date 4/30/96

Subject CONT. FROM PAGE 118

PROCEDURE:

① RUN STAGE I BATCH RXN USING 2X THE AMT. OF MATERIAL.

68.4 gR. SUCROSE
300 gR. ESTER
2.8 gR. GRANULAR K_2CO_3
40 gR. SOAP (K+ STEARATE)

- RUN MINIMUM OF 2 HOURS.

② ADD STAGE II MATERIAL

400 gR ESTER
2.8 gR. GRANULAR K_2CO_3

③ RUN STAGE II UNTIL 15 MINUTES INTO TURBID PHASE

④ FILTER STAGE II MATERIAL THRU 2 WHATMAN GLASS MICROFIBER FILTERS (934-AH) INTO THE COLUMN POT VESSEL.

- SET PRESSURE ON COLUMN & POT TO 50-70 mmHg BEFORE FILTERING. & TURN N_2 ON TO POT 1-3 SETTING.

⑤ TURN ON POT HEATING MANTLE & BEGIN HEATING TO DESIRED TEMP. W/ AGITATOR SET AT 6-7

⑥ WHEN AT DESIRED TEMP TURN ON RECIRC. LINE HEAT TAPE & BEGIN RECIRCULATION AT DESIRED RATE.

⑦ SET COLUMN TO DESIRED PRESSURE

⑧ ADJUST N_2 FLOW TO POT

⑨ READJUST COLUMN PRESS. IF NEEDED.

⑩ AS MATERIAL GETS THICKER N_2 TO COLUMN WILL NEED TO BE ADJUSTED DOWN.

⑪ AT END OF RXN. PUMP ~~IT~~ SYSTEM EMPTY

⑫ RINSE W/ TOULENE

⑬ RINSE W/ METHANOL.

⑭ SHUT EVERYTHING OFF.

Worker's Signature [signature] Date 5/3/96

Corroborating Witness _____ Date _____

120 Date 4/30/90

Subject CONT. FROM Pg. 18

EXPERIMENT:

① CONDITIONS FOR RUN 265°F & 15mmHg.

TIME ZERO 1:15

:45	°F	PLACE	PRESSURE	
	265	TOP	15mmHg	RELIEF SPEED 100%
	243	MIDDLE	—	HEAT LAMP SET @ 55
	243	BOTTOM	30mmHg	HEAT TRACING SET @ 82
:45	267	TOP	15mmHg	HEAT TRACING @ 88.5
	250	MID.	—	
	246	BOTTOM	33mmHg.	
3:45	265	TOP	15mmHg.	HEAT TRACING @ 88
	250	MID.	—	
	248	BOTTOM	33mmHg.	

- AFTER TAKING READINGS DROPPED PRESS TO 5mmHg ON TOP WHICH YIELDED 18 mmHg. ON BOTTOM.
- RXN NOT GOING WELL SO DROPPED PRESSURE!

5:30 SHUT SYSTEM DOWN:

RESULTS:

				42% MC (CALC)
END OF BATCH BEFORE FILTERING	$\bar{I}$ = 5.92		SUCROSE 0.72%	13.9% OCTA
			% MC (CALC)	
T=0 (1:15)	$\bar{I}$ = 5.85	% OCTA = 12.4		43.5
T=0.5 (1:45)	$\bar{I}$ = 5.86	% OCTA = 13.2		40.1
T=1.0 (2:15)	$\bar{I}$ = 6.00	" = 15.3		41.6
T=1.5 (2:45)	$\bar{I}$ = 5.91	" = 12.8		39.6
T=2.0 (3:15)	$\bar{I}$ = 6.03	" = 14.0		35.4
T=2.5 (3:45)		" =		39.0
T=3.0 (4:15)	$\bar{I}$ = 6.01	" = 14.1		34.9
T=3.5 (4:45)	$\bar{I}$ = 6.12	" = 13.4		34.1
T=4.0 (5:15)	$\bar{I}$ = 6.19	" = 15.0		36.2

IT IS MY OPION THAT THE ESTERS USED WERE BAD

Worker's Signature [signature] Date 5/3/90

Corroborating Witness _____ Date _____

Date 5/1/90

Subject PACKED COLUMN EXPERIMENT # 2

PURPOSE : SEE PAGE 118

MATERIALS : SEE PAGE 118

NOTE : USED A DIFFERENT DRUM OF I-85 ESTERS WHICH HAD NEVER BEEN OPENED.

EQUIPMENT : SEE PAGE 118

PROCEDURE : SEE PAGE 119

EXPERIMENT :

CONDITIONS FOR RUN 275°F, 50mm Hg, 8.5:1 ESTER TO SUCROSE RATIO.

N_2 MICROMETER VALVE SETTING AT BEGINNING OF RUN SET AT 6.0 & GRADUALLY THROUGHOUT RUN WAS TURNED DOWN TO 2.5

RECIRC PUMP SPEED AT 6.0 THROUGHOUT RUN

RECIRC HEAT TAPE AT 92 AT BEGINNING OF RUN & GRADUALLY DOWN TO 86 BY END OF RUN.

TIME ZERO 1:00pm

SHUT SYSTEM DOWN AT 5:00pm.

NOT ENOUGH PRODUCT TO FILL COLUMN & RECIRC. LINES AT 2X TIMES NORMAL 1 LITER BATCH.

RESULTS:

				% Me = 30.2
BEFORE FILTERING	SUCROSE = 0.75%	$\bar{I}$ = 5.45	% OCTA = 9.5	% Me (CALC)
T = 2.0 (3:00pm)	$\bar{I}$ = 7.31	% OCTA = 52.2		14.7
T = 3.0 (4:00pm)	$\bar{I}$ = 7.41	" = 59.5		16.0
T = 4.0 (5:00pm)	$\bar{I}$ = 7.53	" = 65.8		11.4

Worker's Signature [signature] Date 5/3/90

Corroborating Witness _____ Date _____

122 Date 5/2/90

Subject PACKED COLUMN EXPERIMENT #3

PURPOSE : SEE PAGE 118

MATERIALS : SEE PAGE 121

EQUIPMENT : SEE PAGE 118

PROCEDURE : SEE PAGE 119

EXPERIMENT :

1) USED A LARGER STAGE I BATCH
   91.2 g/l. SUCRISE
   410 g/l. ESTER
   3.73 g/l. GRANULAR CARBONATE
   53.33 g/l. SOAP (K^+ STEARATE)
2) CONDITIONS FOR RON.
   5 mM H/g., 275°F, 6.5 on RECIRC. RATE
   RUN STARTED W/ 1.5 IN N_2 MANOMETER GAGE & EVENTUALLY
   DOWN TO 0.5
3) TIME ZERO 2:30 PM
   SHUT SYSTEM DOWN @ 7:30 pm.

RESULTS:

			26.1% Me
AFTER FILTRATION	$\bar{I}$ = 5.87	% OCTA = 15.9	% Me (CALC.)
T = 2.0 (4:30)	$\bar{I}$ = 6.71	" = 30.7	16.7
T = 3.0 (5:30)	$\bar{I}$ = 7.09	" = 42.8	14.1
T = 4.0 (6:30)	$\bar{I}$ = 7.12	" = 43.3	17.1
T = 5.0 (7:30)	$\bar{I}$ = 7.22	" = 47.8	16.9

Worker's Signature [signature] Date 5/3/90

Corroborating Witness _____ Date _____

Date 5/4/90

Subject PACKED COLUMN EXPERIMENT # 4

PURPOSE : SEE PAGE 118

MATERIALS: SEE PAGE 121

EQUIPMENT : SEE PAGE 118

PROCEDURE : SEE PAGE 119

EXPERIMENT :

1) USING A LARGER STAGE I BATCH SIZE
   91.2 gm. SUCROSE
   400 gm. ESTER
   3.73 gm. GRANULAR CARBONATE
   53.33 gm. SOAP (K+ STORATE)
2) CONDITIONS FOR RUN
   275°F, 50 mmHg, 8.5:1 ESTER TO SUCROSE
   (REPEAT OF EXP #2 W/ LARGER VOLUME)

8:00AM STAGE I UP TO TEMP W/ FULL VACUUM
10:30 AM ADDED STAGE II MATERIALS
   280 gm ESTER
   5.5 gm. GRANULAR CARBONATE
1:00PM FILTERED STAGE II MAT'L INTO COLUMN POT & BEGAN HEATING TO 275°F
1:30PM COLUMN (TOP) @ 50 mmHg & UP TO TEMP 265 & RISING ROTOR TO 45 TIME = 0 N_2 MICROMOTOR SET @ 4.0
2:00PM 276°F (TOP) 123°C (MIDDLE) 109°C (BOTTOM)
   51 mmHg " — 68 mmHg "
   RELIEF HEAT TRACING @ 92 PUMP @ 6.0
3:30 274°F (TOP) 125°C (MID) 105°C (BOTT) HEAT TRACING @ 89
   50 mmHg Hg " — 71 mmHg " N_2 @ 2.0

Worker's Signature JWRATH Date 5/4/90

Corroborating Witness _____ Date _____

124 Date 5/4/90

Subject Cont. from pg. 123

5:00 Loosing Reflux due to no volume in pot.
- Fluid appears to be very thick & hanging up in column
Reflux down to 2.5 to maintain level & flow.
- Temp fluctuating between 265°F & 280°F. 50 mm Hg
- Mid column temp down to 110°C
- Low column " " " 81°C 72 mm Hg
- Heat Tape @ 75
6:15 - Shut System Down.

Results:

			%Mc (calc.)
Hour T = 0 (1:30)	$\bar{I}$ = 6.14	%OCTA = 19.8	24.2
T = 3.0 (3:30)	$\bar{I}$ = 7.05	" = 43.7	15.1
T = 4.0 (5:30)	$\bar{I}$ = 7.49	" = 63.2	15.9
T = 4.75 (6:15)	$\bar{I}$ = 7.61	" = 72.7	10.1

Composite Sample I = 7.57 %OCTA = 67.5 ~ 18%
- Summited for DFK WSA 001 DFK 40 ppm

Worker's Signature [signature] Date 6/4/90

Corroborating Witness _____ Date _____

Date 5/7/90

Subject PACKED COLUMN EXPERIMENT #5

PURPOSE: SEE PAGE 118

MATERIALS: SEE PAGE 121

NOTE: I-85 ESTERS USED WERE FROZEN & FROM E-90911

EQUIPMENTS: SEE PAGE 118

PROCEDURE: SEE PAGE 119

EXPERIMENT:

1) STAGE I SIZE (SEE PAGE 123 EXPERIMENT 1))

2) CONDITIONS FOR RUN

275°F, 200 mmHg, 8.5:1 ESTER TO SUCROSE RATIO

8:00 AM STAGE I @ TEMP 275°F & FULL VACUUM

11:00 AM ADDED STAGE II MATERIALS

- 280 gr ESTER
- 5.5 gr GRANULAR CARBONTE

12:45 pm - FILTERED STAGE II MAT'L INTO COLUMN POT & BEGAN REHEATING TO 275°F

2:00 T=0 COULD ONLY GET 150mmHg. BUT 1ST FLOOR CLOUDED UP W/ THE LARGE AMT. OF N_2 GOING TO DRAIN SO RESET PRESSURE TO 50mmHg.

3:00 T=1.0 273°F (TOP) 124°C (MID) 107°C (BOTTOM)

51mmHg " — 71mmHg "

HEAT TAPE ON 89 N_2 MICROMETER VALVE @ 2.8

4:00 T=2.0 271°F (TOP) 121°C (MID) 106°C (BOTTOM)

51mmHg " 70mmHg "

SHUT SYSTEM DOWN & SAMPLED & LEFT MAT'L IN POT FOR RE-START 5/8/90

Worker's Signature [signature] Date 5/7/90

Corroborating Witness _____ Date _____

126 Date 5/8/90

Subject CONT. FROM PAGE 125

12:00 NOON. RESTARTED MAT'L FROM 5/7/90

12:45 UP TO TEMP. T=2.0

275°F (TOP.) 122°C (MID.) 103°C (BOTTOM)

52 MM Hg " — 72 MM Hg "

N_2 MICROMETER SET @ 2.3 HEAT TAPE @ 90

RECIRC PUMP SETTING @ 6.0

2:45 T=4.0

275 °F (TOP) 12.5 °C (MID) 109 °C (BOTTOM)

52 MM Hg " — 73 MM Hg (BOT.)

N_2 SET @ 2.3 98.5 HEAT TAPE @

3:45 T=5.0 SHUT DOWN SYSTEM / LEFT MAT'L IN POT UNDER N_2 BLANKET

RESULTS.

	TIME	$\bar{I}$	%OCTA	≃ %Me (CALC.)
	T=0	6.20	20.1	18.2%
RESTART →	T=2.0	6.66	27.9	—
	T=4.0	6.86	32.2	11.8%
	T=5.0	6.87	32.2	13.6%

Worker's Signature [signature] Date 5/9/90

Corroborating Witness _____ Date _____

Date _____

Subject _____

Worker's Signature _____ Date _____

Corroborating Witness _____ Date _____

128 Date 5/22/90

Subject 15 TRAY COLUMN EXPERIMENT # 1

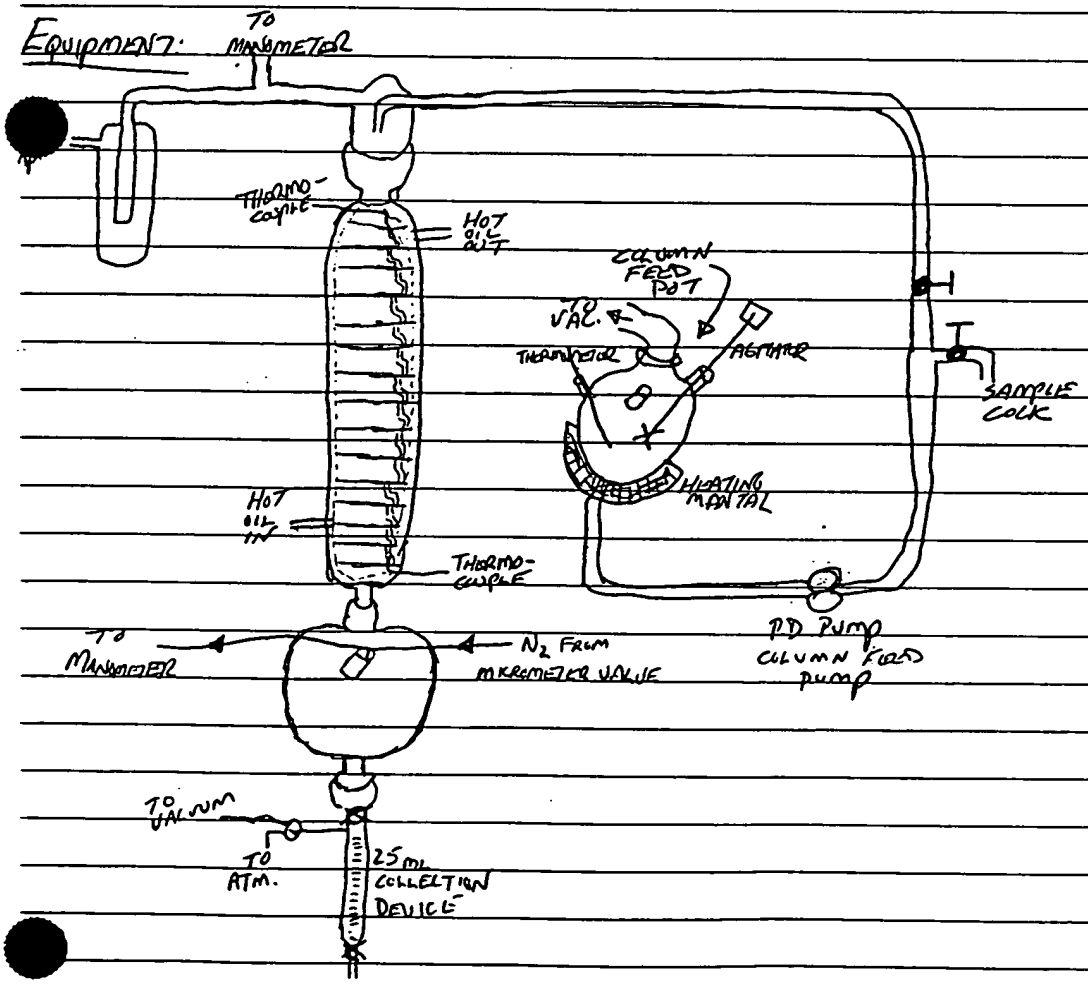
PURPOSE:

TO PRODUCE AT LEAST 75% OCTA BY USING A 15 TRAY COLUMN FOR THE STAGE II REACTION ON A SINGLE PASS THRU THE COLUMN

MATERIALS:

	STAGE I	STAGE II
① GRANULAR CARBONATE	5.0 gr.	5.0 gr.
② I-85 ESTERS E-9091I	400 gr.	400 gr.
③ TWICE GROUND SUCROSE	91.2	—
④ K^+ SOAP	53.3	—

EQUIPMENT:



Worker's Signature [signature] Date 5/22/90

Corroborating Witness _____ Date _____

Date 5/22/90

Subject Cont. from 128

PROCEDURE:

① RUN STAGE I WITH MAT'LS (FROM PG. 128) FOR 3.0 HOURS AT 275°F & FULL VACUUM.

② ADD STAGE II MAT'LS. (FROM PG. 128) AND AT 275°F AND FULL VACUUM

- STOP STAGE II 15 MINUTES INTO THICK PHASE.

③ FILTER THE STAGE II MAT'L INTO THE COLUMN FEED POT THRU 2 WHATMAN GLASS MICROFIBER FILTERS (934-AH

④ SET TEMP. ON THE COLUMN FEED POT TO 50°C & START AGITATOR

⑤ SET VACUUM ON COLUMN TOP & COLUMN FEED POT TO DESIRED SETTING.

⑥ TURN ON HOT OIL SYSTEM TO COLUMN JACKETS TO 145°C

⑦ SET N_2 TO 8 psi (LINE PRESSURE) AND DESIRED FLOW-R. ON ROTAMETER & MICROMETER VALVE

⑧ TURN ON COLUMN FEED PUMP TO DESIRED RATE AND BEGIN FEEDING COLUMN.

EXPERIMENT:

- USED THE PURCHASED K^+ STEARATE FOR SOAP.
- MATERIAL WOULD NOT FILTER SO DECIDED TO RUN THRU THE COLUMN UNFILTERED. $\bar{I}$ OF STAGE I = 6.00 OLEA = 15.5% + 28.6% Me (CALC)
- COLUMN PARAMETERS
  1) ROTAMETER 8 psi (LINE PRESS.) S.S. BAL @ 108 & MICROMETER VALVE OPEN TO 10.0
  2) 10:1 ESTOR TO SUCROSE RATIO .75:1 SOAP:SUCROSE
  3) FEED PUMP SET @ 3.5
  4) 31mm Hg @ TOP OF COLUMN

RESULTS: $\bar{I}$ LOCTA %
END OF TEST. 7.00 42.1 &

- NO VACUUM ON FEED POT.
  - ∴ PRODUCT FOAMING BACK AT TOP OF COLUMN.
- SILICONE GREASE PLUGGED UP DOWN-LEG FROM TRAY 1-2 & 2-3 AND ∴ SHUT SYSTEM DOWN TO CLEAN IT OUT.

Worker's Signature [signature] Date 5/22/90

Corroborating Witness _____ Date _____

Date 5/23/90

130
Subject 15 TRAY COLUMN EXPERIMENT #2

PURPOSE: SEE PAGE 128

MATERIALS: SEE PAGE 128

EQUIPMENT: SEE PAGE 128

PROCEDURE: SEE PAGE 129

EXPERIMENT:

① USED LAB MADE I-1 K^+ SOAP. .75:1

② ESTOL TO SUCROSE 10:1

③ STAGE T RAN A LITTLE SLOW + FILTERED O.K. @ 12:15.

④ EXPERIMENT #1 PARAMETERS.

- 8 psi N_2 (LINE PRESS) 107.5 ON ROTAMETER + 10.0 ON MICROMETER VALVE
- HOT OIL SET TO 145°C
- FEED POT UNDER VACUUM & SET @ 50°C
- FEED RATE TO COLUMN WAS 71-79 DROPS/MIN.
- 34 mm Hg (TOP OF COLUMN) 84 mm Hg (BOTTOM OF COLUMN)
- BOTTOM COLUMN PRODUCT TEMP VARIED FROM 175 TO 185°C THROUGHOUT THE RUN.
  - HIGHER DROPS/MIN RATE THE HIGHER THE TEMP. & VICE-VERSA
- RATE OF PRODUCT EJECTED AT COLUMN BASE
  1) START-UP. 210 mL/hr.
  2) LINED-OUT. 54 TO 66 mL/hr. WHILE LINED OUT.
- CHANGED OVER TO EXP. #2 @ 2:15 T=2.0

⑤ EXPERIMENT #2 PARAMETERS.

- SAME AS EXP #1 EXCEPT N_2 FLOW RATE WAS INCREASED TO 140 ON ROTAMETER + 20 ON MICROMETER VALVE
- 38 mm Hg (TOP) 95 mm Hg (BOTTOM)
- 167°C TO 178°C TEMP. OF PRODUCT AT BOTTOM.
- EVERYTHING ELSE SAME AS EXPERIMENT #1 SHUT DOWN @ 5:30

Worker's Signature [signature] Date 5/23/90

Corroborating Witness Date

Date 5/23/80

Subject Cont. from Pg. 130

Results:

① 66 ml of Product ~~Recovered~~ Collected from Column at Shut-Down. ∴ ≅ 1 hour Residence Time.

%Me (calc.)	Sample	$\bar{I}$	% OCTA	
26.3	Before Filter	5.61	14.2	
32.0	After Filter	5.94	16.9	
35.1	Sample #1	6.06	15.6	Column Just Fu
21.3	" #2	6.03	18.6	5 min. After Ful
	T=2.0 2:15 End of Exp #1	7.00	42.1	
27.3	T=1.5 4:00 pm Exp. #2	6.11	20.7	
1.3	T=3.0 5:30 "	6.63	35.3	

Submitted 5:30 T=3.0 Exp. #2 Sample to Analytical for Low Level Methyl Esters Result 2.1% Me

Comments:

1) T=2.0 Exp. #1 Esters Peaks $\frac{1}{2}$ total area of ISTD Pe
T=3.0 " #2 " " $\frac{1}{3}$ " " " " "

2) Reinc. pump not very reliable at controlling a steady Feed Rate to top of Column.

Worker's Signature SWRAtA Date 5/23/80

Corroborating Witness _____ Date _____

132

Date 5/24/90

Subject 15 TRAY COLUMN EXPERIMENT #3

PURPOSE : SEE PAGE 128

MATERIALS : SEE PAGE 128

NOTE: STAGE I IS THE SAME
STAGE II ESTER INCREASE TO 14:1 MOLE RATIO
OR 720gR / STAGE II

EQUIPMENT: SEE PAGE 128

PROCEDURE : SEE PAGE 129

EXPERIMENT:

① STAGE I RAN O.K. & FILTERED O.K.

② TIME ZERO FOR THE COLUMN @ 12:30pm

③ 145°C HOT OIL BATH TEMP.

④ 278°F (TOP) + 185°F (BOTTOM)
8psi ON N_2 LINE PRESS. 18 ON MICROMETOR VALVE 107.5 ON ROTO.
35mmHg (TOP) 87mmHg (BOTTOM)
2.2 ON FEED PUMP.
50°C SET POINT ON POT TEMP
86 DROP/MINUTE FEED TO COLUMN
8mL/5MIN. TAKE OFF.

2:00 271°F (TOP) 173°F (BOTTOM)
2.5 ON FEED
35mm Hg (TOP) 89 mm Hg (BOTTOM)
ALL OTHER PARAMETERS THE SAME

2:30 CHANGE N_2 TO 5.0 ON MICROMETOR & READING 78 ON ROTAMETER
228°F @ TOP & 248°F BOTTOM
PUMP @ 2.5
3.0mL TO 23 mL IN 1MIN. 40 sec. TAKE OFF
32mm Hg (TOP) 97mm Hg @ (BOTTOM)

Worker's Signature [signature] Date 5/24/90

Corroborating Witness _____ Date _____

Date 5/24/90

Subject CONT. FROM PAGE 132

3:15 242°F (TOP) 242°F (BOTTOM)
32 mm Hg (TOP) 76 mm Hg "
PUMP @ 2.5
5 mL TO 25 mL IN 1 MIN 50 SEC. TAKE OFF.
SAMPLED T = 2.45

3:30 SHUT COLUMN DOWN & 72 mL REMAINING IN COLUMN.

RESULTS.

	$\bar{I}$	% OCTA	% Me (CALC)
T = 1.0 (1:30pm)	7.81	86.9	24.0
T = 2.0 (2:30pm)	7.93	95.9	7.7
T = 2.45 (3:15pm)	6.65	27.9	24.1
T = 3.0 (3:30pm)	6.69	28.5	27.4
BEFORE FILTRATION	6.19	22.7	24.4
AFTER "	6.15	21.8	24.0

COMMENTS:

① HAD A EVACUATION OF BLG. @ 1:00pm. & I BELIEVE FEED SLOWED WAY DOWN!

② FEED WOULD NOT MAINTAIN STEADY FLOW BETWEEN 1:30 & 2:30 & QUESTION: T = 1.0 & T = 2.0 RESULTS.

T = 0 TO T = 2.0 COMPOSITE SAMPLE SUBMITTED FOR DFK #NSA 002
- $\bar{I}$ = 7.93 % OCTA = 94.3 DFK = 784

Worker's Signature [signature] Date 5/24/90

Corroborating Witness _____ Date _____

134

Date 5/31/90

Subject 15 TRAY COLUMN EXPERIMENT #4

PURPOSE: SEE PAGE 128

MATERIALS: SEE PAGE 132 (MATERIALS) FOR WEIGHT.
NOTE: USED IMF ESTERS INPLACE OF THE I-85 ESTERS

EQUIPMENT: SEE PAGE 128

PROCEDURE: SEE PAGE 129

EXPERIMENT:
① STAGE I UP TO TEMP 275°F & FULL VACUUM @ ≈ 7:00AM
② STAGE II MATERIALS ADDED AT 10:00AM
③ FILTERED @ 11:50AM
④ TIME ZERO (T=0) 12:30PM

12:30 270°F (TOP) 205°F (BOTTOM)
≈ 120 DROPS/MIN
8 psi ON N_2 & 10 ON MICROMETER VALVE 107.5 ROTOMETER
FEED POT TEMP SET TO 50 CURRENTLY @ 62
HEAT TRACING SET @ 37
34 mmHg (TOP) 82 mmHg (BOTTOM)
FEED PUMP (TUBING) READING 3.7 & 110 ON DIAL.

1:00 270°F (TOP) 205°F (BOTTOM)
34 mmHg (TOP) 82 mmHg "
FEED POT @ 60°C
FEED PUMP 3.7
3.6 ML TO 24.6 ML IN 10 MIN. 21 ML/10 MIN = 126 ML/HOUR
HEAT TRACING @ 40
117 DROPS/MIN

Worker's Signature [signature] Date 5/31/90

Corroborating Witness _____ Date _____

2:00 271°F (TOP) 202°F (BOTTOM)
34 mmHg " 82 mmHg "
FEED POT SET POINT = TEMP 60°C
ALL OTHER READINGS SAME AS 1:00PM

2:45 SLOW DOWN FEED PUMP. 2.3 READING. 1.04 DIAL SETTING.
80 DROP/MIN.
273°F (TOP) 188°F (BOTTOM)
34 mmHg " 82 mmHg "

3:45 POLLED SAMPLE 3.25
4:30 SHUT DOWN SYSTEM
COMMENTS:
① FLOW FROZE TO FEED PUMP @ ≃ 4:00. THERE WAS NO 4:30 SAMPLE POLLED.
②

RESULTS:	I	% OCTA	% Me (CALC)
BEFORE FILTER	6.28	23.0	38.8
AFTER FILTER	6.27	21.0	39.7
T = 1.0 (1:30)	7.85	86.5	24.1
T = 2.0 (2:30	7.97	98.0	16.7
T = 3.25 (3:45)	7.98	98.8	15.2

T = 0 TO T = 2.0 COMPOSITE SUBMITTED FOR DFK #SA 003
$\bar{I}$ = 7.78 % OCTA = 83.1 DFK = 163

Worker's Signature [signature] Date 5/31/80

Corroborating Witness _____ Date _____

6 Date 6/1/90

Subject 15 TRAY COLUMN EXP #5

PURPOSE: SEE PAGE 128

MATERIALS: SEE PAGE 132 (MATERIALS) FOR WEIGHTS
NOTE: IMF ESTERS USED INPLACE OF I-85

EQUIPMENT SEE PAGE 128

PROCEDURE: SEE PAGE 129

EXPERIMENT:
① STAGE I UP TO TEMP & FULL VACUUM @ 7:30
② FLOODED STAGE II @ 10:45
③ 12:00 NOON COLUMN FULL
④ 12:30 TIME ZERO T=0
⑤ CONDITIONS

:30 N_2 = 8psi 10 ON RECIRCULATOR VALVE 107.5 ON RECIRCULATOR
FEED POT TEMP SET POINT 60°C
FEED PUMP (TUBING) READING 3.7 ≅ 120-124 DROPS/MIN
145°C HOT OIL TEMP.
HEAT TRACING @ 45
34mmHg (TOP) 84mmHg (BOTTOM)
270°F (TOP) 207°F (BOTTOM)

1:30 N_2 (SAME)
271°F (TOP) 204°F (BOTTOM)
35mmHg " 84mmHg "
121 DROPS/MIN
8mL TO 16 mL IN 5 MIN. = 96mL/HR DISCHARGE RATE OF COLUMN
ALL OTHER READINGS SAME AS 12:30

Worker's Signature [signature] Date 6/1/90

Corroborating Witness _____ Date _____

2:38 All Readings Identical to 1:30 except 119 drop/min

3:00 Mtg. w/ G.A.B. & C.B.K

- Emptied collection container every 15 min.

4:30 T=4.0 Shut System Down.

Results:	I	% OCTA	% Me(cal.
Before Filter.	5.89	17.8	31.1
After "	5.74	14.1	30.3
T=0 (12:30)	6.99	38.6	19.6
T=0.5 (1:00)	7.11	47.8	21.1
T=1.0 (1:30)	7.32	50.6	22.8
T=1.5 (2:00)			
T=2.0 (2:30)	7.32	57.1	15.0
T=3.0 (3:30)	7.39	59.8	16.7
T=4.0 (4:30	7.23	52.0	22.4

Comments:

① Column Feed Very Steady Flow & Consistant

② During State I (1st 40 min.) Temp. of Reaction Mix went up to 145°C

- Reaction went fast
- Color was much darker than usual

Worker's Signature [signature] Date 6/1/98

Corroborating Witness _____ Date _____

138 Date 6/4/90

Subject 15 TRAY COLUMN EXP. #6

PURPOSE: SEE PAGE 128

MATERIALS: SEE PAGE 132 (MATERIALS) FOR WEIGHTS.
NOTE: IMF ESTERS USED INPLACE OF I-85

EQUIPMENT: SEE PAGE 128

PROCEDURE: SEE PAGE 129

EXPERIMENT:
① STAGE I UP TO TEMP. (135°C) & FULL VACUUM @ 8:00AM.
② ADDED STAGE II MAT'LS @ 10:45
③ FILTERED AT 12:00 NOON
④ TIME ZERO T=0 @ 1:30
- COLUMN FULL & COLLECTED 15 ML OUT OF BASE
- WILL START SAVING MATERIAL @ 2:00

1:30 272°F (T.P) 204°F (BOTTOM)
35 mmHg " 87 mmHg "
FEED POT TEMP. SET @ 60°C
HEAT TRACING @ 48
8 psi N_2 10 ON MICROMETER VALVE & 107.5 ON ROTOMETER
3.5 READING ON FEED PUMP.
110 DROPS/MINUTE
145°C ON HOT OIL

2:30 273°F (TOP) 199°F (BOTTOM)
35 mmHg " 87 mmHg "
60°C FEED POT TEMP.
ALL OTHER PARAMETERS SAME AS 1:30 112 DROPS/MIN.
9 ML TO 19 ML IN 6 MINUTES COLLECTED AT COLUMN BASE = 100 ML/HR

Worker's Signature K. Allen Date 6/4/90

Corroborating Witness _____ Date _____

Date 6/4/90

Subject Cont. from P6. 138

3:30 272°F (Top) 201°F (Bottom)
35 mmHg " 87 mmHg "
110 drops/min.
All other readings same as 2:30

4:30 274°F (Top) 206°F (Bottom)
Feed pump reading 3.0
Can't see into column head for drip count

5:00 Shut system down.

Results:

	$\bar{T}$	% OCTA	% Me (calc)
Before Filtration	6.27	26.4	31.8
After Filtration	6.22	19.9	25.1
T = 1.0 (2:30)	6.98	38.2	19.0
T = 2.0 (3:30)	6.69	23.8 ?	23.6
T = 3.0 (4:30	6.52	24.2	20.2

Worker's Signature [signature] Date 6/4/90

Corroborating Witness _____ Date _____

RESTRICTED CIRCULATION

RETENTION LIMIT: ORIGINATOR AND LIBRARY - 1/1/95
ALL OTHERS - READ AND OUT

INDUSTRIAL CHEMICALS PRODUCT DEVELOPMENT BIWEEKLY REPORT

J. KAO

PERIOD ENDING FEBRUARY 8, 1989

We've designed a screening study to find out the important FG process variables that contribute to DFK formation. Variables to be studied include KOH level, FFA, carbonyl value, catalyst amount and size, sucrose size, reaction temperature, pressure and feed preparation.

DFK Screening Design

DFK (Difatty Ketone) forms in a parallel reaction competing with FG esterification. The formation rate of DFK, however, is only about one one thousandth of the FG reaction rate. Since 1986, DFK level in finished FG has increased from 100-200 ppm to the current 500-1000 ppm level. At the same time, we've reduced FG reaction time from 30 hours down to the current 7 hours in clinical batch production. Based on our review of clinical batches and a preliminary DFK kinetic study, there is a strong link between FG reaction rate and DFK formation. A fast FG reaction tends to give a higher level of DFK concentration. Probably, some of the changes we made in the past two years to enhance the FG reaction have favored DFK formation even more.

To find out what variables most favor DFK formation, we've designed a screening study to look at all the possible process parameters and to understand the influence of those parameters on both DFK and FG reactions. The experimental results will then be analyzed by Mr. Bob Belanger to identify the statistic significance each variable contributes to DFK formation.

The variables we've initially included in this design are KOH level in the soap, FFA, carbonyl value, catalyst concentration and size, reaction temperature, pressure, sucrose size, soap concentration and feed preparation. The first variable we'll be looking at is KOH level in the soap which can vary from batch to batch. Literature and Dr. Letton's lab experience indicate that strong base is needed for DFK formation. KOH is a stronger base than K_2CO_3 and may be a contributor to DFK formation in FG. Since it can vary, we need to know its influence first so that subsequent experiments can be conducted properly.

It is my opinion that several variables contribute to DFK formation in different degrees. By conducting this screening design and a subsequent DFK kinetic study, the mystery of DFK formation will be resolved. Then, we can expect a more robust FG reaction process and product.

Mr. Jim A. Letton joined us on 2/6/89. He will work on understanding DFK formation chemistry. Please stop by to welcome Jim.

Junan Kao
C2A07 SWTC; Ext. 4478

Keywords: Difatty Ketones, Screening Design.

LABORATORY BOOK NO. SI 1367
ASSIGNED TO J. Kao
TRANSFERRED TO _____ DATE _____

CORRESPONDING LOOSE-LEAF NOTEBOOK TI 0126

DATE ISSUED 6-14-88
DATE RETURNED 8-11-93
SUBJECT _____

BS
S.W.I.C.

INSTRUCTIONS FOR ENTERING DATA IN LABORATORY NOTEBOOKS.

LABORATORY NOTEBOOKS ARE LEGAL DOCUMENTS. NOTEBOOKS NOT COMPLYING WITH SPECIFICATIONS MAY BE RETURNED FOR CORRECTION. SEE "A GUIDE TO THE USE OF LABORATORY NOTEBOOKS" FOR ADDITIONAL INFORMATION.

DATA ENTRIES

A. Enter data into the notebook as the work is being performed. Entries should be made in black ink only. DO NOT USE PENCIL to enter data in notebook. Enter the date the work is started at the top of the page. Enter the title of the work on the top line immediately following the date.

B. Describe the purpose of the work, give a narrative description of what was done, and indicate the sequence in which each step was taken. Cross Reference data entries as appropriate for maximum clarity. For example, if analytical results on coded samples are entered in the notebook, enter the notebook and page number where the sample description can be found and provide references to procedures or analytical methods used.

C. Define trade-named materials, acronyms or jargon, the first time they are used. Show the mathematical formula for all calculations and a sample calculation if the principle is not obvious. Computer programs used for data analysis should be referenced.

D. Enter factual results only. These include data as well as observations. Opinions should not be recorded in the notebook. Comments implying failure should be avoided.

E. Make entries on a given subject on consecutive pages where practical. Restrict each page to a single subject or test. When considerable work on a single subject is to be done, reserve a single notebook for the work whenever practical.

F. Do not skip pages. When unavoidable, cross through blank page(s) in ink, initial and date. Blank partial pages should also be crossed through in ink, initialed and dated.

G. Do not erase or use correction fluid in notebooks. When corrections are necessary:
   1. Cross out the original entry such that it remains legible;
   2. Enter the correction along with an explanation as to why the correction is necessary; and
   3. Date and initial the correction.

H. DO NOT USE HIGHLIGHTER.

ATTACHMENTS

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Date February 21, 1989

Subject DFK screening study, KOH variation

Purpose: To see the level of KOH concentration to the FG & DF-K reaction

Reaction

	Sucrose	+ IMF	+ K_2CO_3	+ K^+ soap (1.1% KOH)
M.W.	342	~296	138	322
Mol	.2	2.4	.02	.15
wt	68.4g	296+414g	2.76g	48.3g

Time	Temp. (°C)	Pressure, mHg	Comments
8:10			1) Mix Sucrose, K^+ soap, K_2CO_3 & IMF
8:20	50	0.5	2) Agitate, Vacuum & Heat to 135°C
8:30	135	0.6	stage I reaction, Time 0.
10:00	135	1.0	Add esters & K_2CO_3, Sample JK-107-1
10:10	135	0.8	Heat up to 135°C, stage II, Time 0
11:10	135	0.5	Sample JK-107-2 (2.5 hrs)
			Poor sucrose utilization (a layer of sucrose left)
12:10	135	1.0	A big bubble foaming on the top
			Sample JK-107-3 (3.5 hrs) [slow down agitation]
13:10	135	0.9	Sample JK-107-4 (4.5 hrs)
14:10	135	1.2	Sample JK-107-5 (5.5 hrs)
			* For a baffled reactor, it needs only adequate agitation, too high agitation create circulation and eliminate bubble forming and slow down reaction.
15:10	135	1.0	Sample JK-107-6 (6.5 hrs)
16:10	135	0.8	Sample JK-107-7 (7.5 hrs)
			stop. overnight in a jar
			Sample JK-107-8

Worker's Signature Jun Kun Shue Date 2/22/89

Corroborating Witness J. A. Lofton Date 5/2/89

108 Date February 23, 1989

Subject DFK screening study, KOH variation

Purpose: Repeat of page 107 JK reaction with a proper control of Agitation speed to just keep foaming in the reactor.

Reaction: ↳ 30 dial

	Sucrose	+ IMF	+ K_2CO_3	+ K soap (1.1% KOH)
M.W.	342	~296	138	322
Mol.	.2	2.4	.02	.15
wt.	68.4g	296+414g	2.76g	48.3g

Strategy: To control DFK formation rate by adjusting agitation speed [methanol level & FG reaction: Goal DFK ppm vs Time]

Time	Temp(°C)	P(mmHg)	Comments
7:30			1) Mix sucrose, soap, K_2CO_3 & IMF
7:40	40	0.6	2) Agitate, vacuum & heat to 135°C
8:00	135	0.4	3) Stage I reaction, Time 0.
			Control agitator speed to maintain bubble foaming on the surface. (25-30 dial)
9:30	135	1.1	Add K_2CO_3 & stage II esters, Sample JK-108-1
9:45	135	1.7	4) Stage I reaction, Time 0, bubble violate.
10:45	135	0.8	Sample JK-108-2 (2.5 hrs), poor sucrose utilization
11:45	135	1.0	Sample JK-108-3 (3.5 hrs)
12:45	135	0.9	Sample JK-108-4 (4.5 hrs), bubble violent, dial=33
13:45	135	0.8	Sample JK-109-5 (5.5 hrs)
13:50	135	0.8	5) Increase agitation speed, dial=45, no foaming,
14:45	135	0.7	Sample JK-109-6 (6.5 hrs), no foaming
15:45	135	0.7	Sample JK-109-7 (7.5 hrs), no foaming
15:50	135	0.7	6) Decrease agitation, dial=30, foaming on top
16:45	135	1.1	Sample JK-109-8 (8.5 hrs), foaming dial=35
17:45	135	1.3	Sample JK-109-9 (9.5 hrs), foaming dial=30
			overnight
9:45	25		Sample JK-109-10

Worker's Signature Jin-Kun Hwu Date 2/24/89

Corroborating Witness J. A. LaVoie Date 5/12/89

Date March 2, 1989

Subject DFK Screening Study, Pressure

Purpose: FG reaction for DFK Screening Study with a constant pressure of 3 mmHg.

Reaction:

	Sucrose	+ IMF	+ K_2CO_3	+ K⁺soap (@14% KOH)
M.W.	342	~296	138	322
Mol.	.2	2.4	.02	.15
wt.	68.4g	296+94g	2.76g	48.3g

Time	Temp.(°C)	P(mmHg)	Comments
8:00	20		1) set up Cartesian Manostats and operate under vacuum at P= 3 mmHg. to check the system.
8:00	40	3	
			2) Add Sucrose, IMF, K_2CO_3, K⁺soap, Agitate
8:30	70	3	Vacuum & heat to 135°C maintain P=3 mmHg
8:40	135	2.8;3.0	3) Stage I, Time 0, Dial = 30
9:45	135	3.0	Severe foaming Dial= 35.
10:15	135	3	Sample JK-111-1 (1.5 hrs) [Add ME & K_2CO_3]
10:20	110	3	Foaming severe, clear, good sucrose utilization, Brown
10:30	135	3	4) Stage II, reaction, Time 0, Dial back to 30
			Reaction fast (bubbling), Pressure increase to 4-5
			because of fast bubbling, turn dark brown clear
11:30	135	5	Sample JK-111-2 (2.5 hrs) Turn cloudy, Dial = 35
12:00	135	3.6	Total cloudy, Brown, Dial = 30
12:30	135	3.4	Sample JK-111-3 (3.5 hrs), bubbles gone
13:30	135	3.0	Sample JK-111-4 (4.5 hrs)
14:30	135	2.9	Sample JK-111-5 (5.5 hrs)
15:30	135	3.0	Sample JK-111-6 (6.5 hrs)
16:30	135	2.8	Sample JK-111-7 (7.5 hrs)
17:30	135	3.4	Sample JK-111-8 (8.5 hrs)
18:30	135	3.0	Sample JK-111-9 (9.5 hrs) stop.

Worker's Signature Jy-Nan Hwu Date 3/2/89

Corroborating Witness J. A. LeMon Date 5/12/89

LABORATORY BOOK NO. SI 1367
ASSIGNED TO J. Kao
TRANSFERRED TO _____ DATE _____

CORRESPONDING LOOSE-LEAF NOTEBOOK TI 0126

DATE ISSUED 6-14-88
DATE RETURNED 8-11-93
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S.W.I.C.

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136

Date May 9, 1989

Subject FG reaction at a lower temperature.

Purpose: To find out what is the minimum temp. for FG reaction the second stage and possible prevention of DFK formation.

Reaction

Sucrose + K_2CO_3 + K'soap + Esters (R90302) → FG 490.8g

68.4g 27.6g 4.3g 296+118+118+59+59+59

0.2

135°C 120°C 100°C 100°C

Time	T(°C)	P(mmHg)	Comments JK using 120°C the second stage
7:30			1) Add sucrose, K_2CO_3, K'soap & esters
7:40			2) Mix, agitate, heat and vacuum to 135°C.
8:00	135	0.3	3) Stage I, Time 0
9:30	135	0.8	Sample JK-136-1 (1.5 hrs) (light clear solution)
			4) Add K_2CO_3 & 118g esters (
			set T= 120°C
9:50	120	0.7	clear phase, bubbling.
10:30	120	1.1	still clear phase, bubbling
			Sample JK-136-2 (2.5 hrs), T=120°C
11:30	120	1.7	Sample JK-136-3 (3.5 hrs), bubbling strong
			Turn cloudy phase, add 59g esters
			set T= 100°C (need good sucrose utilization
11:35	100	0.8	Bubbling but not strong so reaction is
12:35	100	0.85	Bubbling Sample JK-136-4 (4.5 hrs) homogeneous)
			Add 59g esters, still bubbling
1:30	100	0.8	Bubbling Sample JK-136-5 (5½ hrs)
			Add 59g esters
2:30	100	0.6	Bubbling Sample JK-136-6 (6½ hrs)
3:30	100	0.2	Bubbling Sample JK-136-7 (7½ hrs)
4:30	100	0.25	Bubbles gone JK-136-8 (8½ hrs)
			Stop & Purify 85% oda, 87 ppm DFK
	Finished	FG	JK-136-9, 300 ppm FG due to poor yield of FG 42%

Worker's Signature [signature] Date 5/9/89

Corroborating Witness [signature] Date 5/12/89

Date May 18, 1989

Subject FG low temp. reaction using wet soap method

137

Purpose: Running FG reaction at 100°C to eliminate DFK formation using wet soap method to insure good sucrose utilization and high yield.

Reaction:

Sucrose + K_2CO_3 + K soap + CH_3OH + Ester (137-18-1) → FG

68.4g 2.76g 98.3g 200 ml 296 + 414g

Time	T(°C)	P(mmHg)	Comments
7:30			1) Add soap with methanol dissolved at 60°C
			2) Add K_2CO_3 & Sucrose
			3) Add esters, set T = 135°C to evaporate CH3OH
8:30	135		4) Place vacuum, First stage reaction
8:40	134	1.6	cream solution
9:15			Turn brown clear, bubbling
10:00	135	1.2	5) Sample JK-137-1, brown clear
			Add K_2CO_3 & stage 2 esters (400g)
10:05	91	0.5	Reaction goes bubbles, clear phase
11:00	100	0.4	Still clear, bubbles
12:30	100	0.6	Bubbling strong, turn cloudy
1:00	100	0.6	6) Sample JK-137-2, (4.5 hrs)
			brown cloudy, bubbling
3:00	100	0.7	7) Sample JK-137-3 (6.5 hrs)
			cloudy phase, bubbling strong
			still long way to go indicated by IR
4:00	100	0.8	bubbling strong
5:00	100	0.8	8) Sample JK-137-4 (8.5 hrs)
			cloudy phase, bubbly severe, Reaction Progress by
6:00	100	0.8	9) Sample JK-137-5 (9½ hrs) bubbling, IR
7:00	100	0.6	10) Sample JK-137-6 (10½ hrs), bubbles (conti only).
8:00	100	0.4	11) Sample JK-137-7 (11½ hrs), stop, overnight
8:55	100	0.4	12) start again, 8.55 (12½ hrs) P = 0.25 mmHg
9:25	100	0.2	Bubbles gone, sample JK-137-8 (13 hrs) stop. Purified JK-137-9 280g, 57%

Worker's Signature J. K. Kundu Date 5/19/89

Corroborating Witness J. A. Fehr Date 6/23/89

144 Date June 12, 1989

Subject FG 100°C Reaction, Wet Soap Method

Purpose: making high octa FG (78.5%) and low DFK.
Operate at 100°C second stage. ½ X catalyst and 2½ hrs first stage reaction.

Reaction:

Sucrose + IMF + K_2CO_3 + K^+soap (CH_3OH) → FG
68.4g 296+44g 2.76g 48.3g 491g

Time	Temp(°C)	P(mmHg)	Comments
			1) Making I-1 soap.
7:30			Add 200 ml CH_3OH, 44.8g I-1 & 9.4g KOH
8:00			Reflux at 60°C for an hour.
8:30			2) Add K_2CO_3 and Sucrose
			Add 296g ME increase T ↗ 135°C.
9:10	135	1.5	3) Vacuum, Stage I reaction time zero.
9:25	135	1.2	Bubble-foaming, cream solution, T=100°C
10:00	135	0.8	clear brown phase ↓
10:40	135	0.7	4) Sample JK-144-1, dark brown (2.5 hrs)
11:40	100 ~~+35 JK~~	0.7	↔ Add 414g IMF-ME.
12:15	100 ~~135 JK~~	0.6	cloudy brown.
1:40	100 ~~135 JK~~	0.7	Sample JK-144-2, (4.5 hrs) brown cloudy
			bubbling, center.
5:40	100 ~~135 JK~~	0.6	bubbling, Sample JK-144-3 (8.5 hrs)
			Overnight
7:40	100	0.5	bubbling
12:20	100	0.25	fewer bubbles
1:40	100	0.2	Sample JK-144-4 (14.5 hrs), 61.6% octa
3:40	100	0.2	no bubbles.
5:40	100	0.15	Sample JK-144-5 (18.5 hrs) DA
7:40	100	0.15	Sample JK-144-6 (20.5 hrs), 75.6% octa
			overnight ↳ Finished FG 525, (ME=278)
7:40	100	0.20	Start again

Worker's Signature J.-Kuen Jue Date 6/14/89

Corroborating Witness J. A. Firth Date 6/23/89

Date June 14, 1989

Subject FG 100°C Reaction, Wet soap Method.

Time	Temp.(°C)	P(mmHg)	Comments.
12:40	100	0.1	Sample JK-144-7 (25.5 hrs)
			Stop
			Finishing sample
			1) Add water & hydrate soap.
			2) Centrifuge to remove soap
			3) Add filtrol (~1%)
			4) Filtration
			5) Evaporation at 240°C, 0.2 mmHg.
			FG — 342 g, JK-144-8
			ME — 213 g -30g = 183 g
			Total FG — 394 g [80% yield]
			ME — 240 g -30 = 210 g
			[89% recover]
			JK-144-6A
			80.7% oda 212 DFK ppm
			JK-144-8
			91.4% oda, 374 ppm DFK.

Worker's Signature [signature] Date 6/14/89

Corroborating Witness [signature] Date 6/23/89

LABORATORY BOOK NO. SI 1386
ASSIGNED TO J. KAO
TRANSFERRED TO _____ DATE

CORRESPONDING LOOSE-LEAF NOTEBOOK _____

DATE ISSUED June 28, 1989
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Date 9/25/89

Subject 5 pph, Batch Reaction

Purpose: Run batch reactions to understand 5 pph system ability and provide information for national design and continuous reaction fundamental study. Including
a) Filtration study
b) Recirculation rate study
c) Sparge tip design
d) Recirculation spray
e) Centrifuge pump test.

Reaction: IMF Blendy esters reaction

Esters (Blend Y, R90503)

- Sucrose (Ground twice)
- Carbonate (Powder)
- Soap (Excess I-1)
- Esters (R90503)

Feed Mix from S90911
Ratio (molar)
1/5.5/.75/.058

Final 1/14/.75/.116

Standard Procedure:

Stage I:

1) Add Feed mix to reactor (4000 ml). [might need 13 g K_2CO_3]
2) Heat up to 275°F and vacuum at 15 mmHg.
3) Keep reaction for an hour after foaming gone.

Stage II:

1) Add 4500 ml esters and 13 g powdered K_2CO_3 to the reactor mix.
2) Bring temp. back to 275°F and full vacuum (~1 mmHg)
3) Nitrogen sparge with Rotameter setting ~15.
4) React for about 4 hrs.

* Sampling at every hour for SFC & sucrose.

Worker's Signature Jin-Kun Lin Date 9/25/89

Corroborating Witness _____ Date _____

CHEMICALS PRODUCT DEVELOPMENT MONTHLY REPORT

J. KAO

PERIOD ENDING NOVEMBER 1, 1989

Farewell to FG! It has been fun for the past 17 months.

5 PPH PILOT PLANT

It has been a great month for the 5 pph pilot plant system. Not only we have shown that the 5 pph system can consistently produce high octa material, but also we have identified some important reactor design factors for FG continuous reaction technology development.

Steve and Nelson ran several batch reactions to study the effects of recirculation rate, nitrogen sparge design and filtration on the FG reaction. The first two items are scale dependent and may be unique to the mixing characteristics of the system.

1) Recirculation rate - a fast recirculation rate gives a consistent FG reaction and reaches high octa. The fast recirculation helps the mixing of the reaction crude and enhances the methanol removal.

2) Nitrogen sparge design - a fine sparge dispenser installed at the bottom of reactor gives a very fine nitrogen bubbles. The fine bubbles enhance the mass transfer and the removal of methanol that push the reaction to completion.

3) Filtration - the filter removes soap, unreacted and burned sucrose, and carbonate solids. These removal dramatically enhances FG reactions. All three reactions we have done that filtered at different I-bars reached 100% octa in two hours after filtration.

5 pph system have proved that the system can consistently produce high octa material (~90% octa) and operate at wide range of operating conditions. A list of data and comparison with the 70 pph system run P90213 is shown as follows:

Run	Soap Level	Temp. °F	P mmHg	% octa	Color
S90911	1	275	1	88	1.0R/4.2Y
S91009-1	1	275	1	89	0.8R/3.2Y
S91009-2	1	265	1	87	1.3R/4.9Y
S91009-3	1	265	3	82	1.3R/4.9Y
S91016-1	1/3	265	1	85	2.9R/13Y
P90213	1	275	2	90	-

Producing high octa material is the first step for the 5 pph system becoming the focus of FG continuous reaction technology development. Next step for the 5 pph system is to implement new technology development update and to fulfil FG development goals.

This report also ends my assignment with olestra process development. I am looking forward to working on new surfactant development. I would like to take this opportunity to thank everyone. It has been fun working with all of you for the past 17 months.

Junan Kao

INDUSTRIAL CHEMICALS PRODUCT DEVELOPMENT BIWEEKLY REPORT

R. G. SCHAFERMEYER PERIOD ENDING FEBRUARY 22, 1989

KOH in soap may be a hidden catalyst in many FG-Base reactions. A dual hydroxide-carbonate catalyst system may explain some of the variations seen between reactions.

HIDDEN CATALYST

While reviewing past clinical batch records looking for leads to explain differences in difatty ketone levels, Ju-Nan Kao noted that KOH levels in soap vary slightly from batch to batch. Since KOH is a stronger base than our catalyst K_2CO_3, it may contribute to the variations in DFK level that we see in Building 96 production. He plans to follow-up this observation with lab experiments.

Upon further reflection, it occurred to me that KOH may be a hidden catalyst for the FG-Base reaction. Current specs for clinical batches call for less than 0.9% KOH in the soap. Most batches of soap have between 0.7 and 0.85% KOH. Since soap is used at the 10% level in stage one, only about 0.08% KOH is added. This might not seem like much, but it increases the total moles of catalyst (defined as KOH and K_2CO_3) by 34%.

For continuous pilot plant reactions, the KOH level in soap is even lower, about 0.2%. On a molar basis, total catalyst increases by only 9%. This lower level of KOH may partly explain the tendency for continuous reactions to run slower than clinical batches.

Another difference between continuous and clinical batch reactions is the start-up methods. In clinical batches, both the KOH and the K_2CO_3 see methanol. John Howie has shown that methanol reduces carbonate particle size; my guess is that it would have the same effect on KOH. In continuous reactions, only the KOH sees methanol. As a result, the KOH may be present as finer particles than the K_2CO_3. Pat Corrigan has shown that particle size is a more important measure of catalyst activity than the weight of catalyst added. This could make KOH the prime catalyst, even though on a molar basis it is present at only 1/10th the carbonate level.

Greater exploration of this area is planned. Defining a narrower spec for KOH in soap may be an appropriate next step. The particle size methods being developed by Dave Maltbie and Bill Hughes will be critical for explaining the effect of KOH and surface area on reactivity. Our efforts to better understand the chemistry of the FG-Base reaction continues to pay dividends.

R. G. Schafermeyer

RGS/elg/1827

Key Words: K_2CO_3, catalyst, KOH, method of addition, particle size, soap making

RESTRICTED CIRCULATION

55

RETENTION LIMIT: ORIGINATOR AND LIBRARY - 1/1/94
ALL OTHERS - READ AND OUT

INDUSTRIAL CHEMICALS PRODUCT DEVELOPMENT BIWEEKLY REPORT

R. G. SCHAFERMEYER

PERIOD ENDING JANUARY 25, 1989

Our understanding of difatty ketone formation is increasing.

DFK KINETICS

A project to minimize difatty ketone (DFK) formation during the FG reaction is underway. Dr. Ju-Nan Kao is spear-heading the effort with his program to measure the kinetics of DFK formation during the FG reaction. Dr. Jim Letton is complementing this work by measuring the kinetics of DFK formation in methyl esters alone (a follow-up to his DFK sample preparation effort).

Our current approach is to consider DFK formation a parallel and competitive reaction to FG esterification. This means that the absolute rate of DFK formation is not as important as the relative rates between esterification and ester condensation. Process changes that affect both reactions equally will not reduce the total amount of DFK at the end of the reaction. Instead, we must learn to control the DFK reaction independently of the FG reaction.

Although we are in the early stages of data collection, we have already made some important learnings:

1. Most of the DFK forms in the second stage of the reaction. In stage 1, DFK forms at an average rate of about 7-100 ppm per hour. In stage 2, it forms at an average rate of about 27-450 ppm per hour, or about four times faster. This makes sense since the catalyst and methyl ester levels in stage 2 are each about twice as high as in stage 1. These rate differences result in about 10-150 ppm of DFK at the end of stage 1 and about 200-2000 ppm at the end of stage 2. Keep in mind that stage 2 is 2-4 times longer than stage 1.

2. For a given run, DFK forms at a constant rate in stage 2. Plots of DFK versus time fit a straight line. This is true for lab, clinical batch, and continuous reactions. This suggests that DFK formation is not limited by ester and catalyst concentrations, which are always high relative to the amount of DFK that forms.

3. The rate of DFK formation varies from run to run. The highest levels are formed in a fast lab reaction using powdered sucrose and catalyst; the lowest levels were formed in a slow continuous reactor run. This suggests that process conditions that favor esterification also favor DFK formation.

4. The longer it takes to achieve a given octa, the lower the DFK level. This behavior was first identified by Ju-Nan as he reviewed clinical batch data. Bob Belanger mathematically confirmed that longer stage 2 reaction times lead to lower DFK levels. A review of recent lab, clinical batch, and continuous reactor data indicate similar behavior. This implies that whatever slows the esterification reaction slows the DFK reaction even more.

Understanding the kinetics of DFK formation is the critical first step in reducing levels in the finished product. I believe we are off to a good start.

R. G. Schafermeyer

RGS/elg/1769

R. G. Schafermeyer

RESTRICTED CIRCULATION

RETENTION LIMIT: ORIGINATOR AND LIBRARY - 1/1/94
ALL OTHERS - READ AND OUT

CHEMICALS PRODUCT DEVELOPMENT BIWEEKLY REPORT

R. G. SCHAFERMEYER

PERIOD ENDING JUNE 28, 1989

Lab and clinical batch samples of FG with low difatty ketone levels have been produced. Consistently controlling DFK to low levels requires greater understanding of the fundamental chemistry.

DIFATTY KETONE

In late 1987, DFK levels in finished FG increased from the 100-200 ppm range into the 300-600 ppm range. This higher level of DFK has persisted, with the last nine months of I85/I8 production at Building 96 averaging 550 ppm. The increase in DFK seems to correlate with the faster reactions and higher conversions that result from the use of stable, high quality feedstocks such as I85/I8.

Even though some recent lots of I85/I8 have DFK levels as high as 1000 ppm, others have DFK as low as 220-300 ppm. These latter lots meet our target of less than 300 ppm DFK at greater than 70% octa:

I85/I8 Lot	Octa	DFK (Finished FG)
C90105	78%	221 ppm
C90131	81	243
C90111	88	303

In addition, Ju-Nan Kao and Jim Letton, Jr. have produced a lab sample with an octa of 79% and only 70 ppm DFK by using a lower stage two temperature. These lab and clinical batch samples demonstrate that high octa/low DFK FG is technically feasible.

The overriding pattern seen in samples with high octa/low DFK is slower stage two reactions. The reaction can be slowed by changing process conditions such as temperature or pressure or by using less ester or catalyst. The difficulty with such an approach is that slow FG reactions frequently hit a wall at 70-80% octa, well below our current product target of 90% octa. Slow reactions also appear more sensitive and less reproducible. We believe this is related to the formation of the "true" catalyst from the added catalyst potassium carbonate. John Howie has some intriguing data showing that minuscule amounts of multiple strong bases can be formed in the FG reaction. Termination of these bases at the end of the reaction may lead to DFK.

Effective July 1, Ju-Nan Kao is moving to a new assignment on the 5 pph continuous reaction system. Jim Letton, Jr. will continue to probe DFK formation, along with John Howie and Larry Noertker who are trying to understand the underlying catalyst system of the FG reaction. The empirical approach used the past six months has uncovered some promising leads, but an understanding of the fundamental chemistry is needed so that we can purposefully control DFK formation. That is our focus for the coming months.

RGS/elg/2092

R. G. Schafermeyer

Keywords: catalyst, difatty ketone

RETENTION LIMIT: ORIGINATOR AND LIBRARY - 1/1/94
ALL OTHERS - READ AND OUT

CHEMICALS PRODUCT DEVELOPMENT DIVISION BIWEEKLY REPORT

R. G. SCHAFERMEYER

PERIOD ENDING SEPTEMBER 6, 1989

The key to reducing DFK formation is to understand its chemistry. The chemical puzzle is being pieced together by Drs. Howie, Letton, and Flynn.

DIFATTY KETONE CHEMISTRY

The difatty ketone (DFK) precursor most likely present in reaction mixtures is beta-keto ester (BKE). BKE forms by the classic Claisen condensation of two esters in the presence of a strong base. The reaction occurs when a base such as methoxide first abstracts a hydrogen atom from the alpha carbon on a methyl ester, forming methyl ester anion (MEA) and methanol. MEA then attacks another methyl ester at the carboxylic carbon, forming BKE and regenerating methoxide ion. Because the BKE still contains a hydrogen atom on the alpha carbon, it is very acidic and reacts with the regenerated methoxide releasing methanol and consuming one equivalent of base. This explains Dr. Letton's observation that stoichiometric amounts of base are needed to generate DFK samples for animal studies.

Other condensations can also occur. Any aldehyde, ketone, or ester having a free alpha hydrogen can initiate the reaction. Perhaps this explains why reactions with high carbonyl contents "hit a wall" near the end of the FG reaction. The more polar aldehydes are attracted to the catalyst surface where they then condense with other aldehydes or esters, in the process consuming base and stopping the reaction.

The consumption of base also supports the termination theory of DFK formation. As the esterification reaction nears the end, there are very few free OH groups available. When the still active base can't find an OH group, it attacks an ester, forming acidic BKE which neutralizes the base and prevents further FG or BKE reaction. This could also explain why fast reactions form more DFK. A fast reaction is fast because more active base has been formed. This greater amount of base eventually terminates into a larger amount of BKE.

All of the condensation reactions are equilibrium reactions that are not thermodynamically favored. They require a driving force to occur to any extent. Unfortunately, the conditions required to force the esterification reaction to high octa (low methanol concentrations created by low vacuum) are exactly the ones that favor ester condensation.

Fortunately, the activation energies of esterification versus condensation appear different, as shown by Dr. Kao's observation that lower stage two temperatures help reduce DFK formation. There may be a temperature at which esterification will proceed but condensation will not. We know that in base-catalyzed triglyceride rearrangements, DFK formation appears to be suppressed at 55C. Can high octa FG be made at the end of the reaction at this temperature without BKE formation? Although the esterification reaction will be slow, it may be possible to manipulate the type and concentration of catalyst to regain lost rate.

R G Schafermeyer

RGS/elg/2225

R. G. Schafermeyer

Keywords: difatty ketones

RESTRICTED CIRCULATION

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CHEMICALS PRODUCT DEVELOPMENT DIVISION - FOOD INGREDIENTS MONTHLY REPORT

R. G. SCHAFERMEYER

FOR PERIOD ENDING 10/1/89

Our objective is to produce FG-Base with less than 300 ppm DFK. We are pursuing four approaches to achieve this objective. A brief description and status report for each approach is given.

DIFATTY KETONE CONTROL

Low Octa Specification. Our data clearly indicate that DFK can be kept below 300 ppm if octa is kept below 80%. In practical terms, octa must be kept below 75% to accommodate analytical and process control variations. The product impact of lower octa is being assessed by Mr. Zimmerman in OPD. The process impact is favorable in that the reaction rate can remain about normal and higher throughput for a given reactor volume can be achieved.

Reaction Variables. Our data indicate that a lower stage two temperature (100°C versus the normal reaction temperature of 135°C) allows us to achieve higher octa (82-84%) while still keeping DFK below 300 ppm. The process impact is unfavorable because the reaction is very slow (requiring additional reactor volume) and because the reaction becomes erratic (tending to hit an octa wall). Even lower temperatures (i.e., 60-80C) have been tested but aren't useful because both the DFK and octa reactions stop. We continue to pursue reduced temperature as a means to control DFK formation.

Continuous reactor data indicate that reduced soap may also lead to lower DFK. This probably occurs from the reduced level of base being added to the reaction. We plan to test residual base and DFK precursor formation in soap making.

Reversion. Several ideas are being explored. One idea was to use low temperature, methanol, and methoxide catalyst to revert DFK to methyl esters. Unfortunately, FG-Base reverts faster than DFK. A second idea involves the use of dialkyl carbonate to react with methyl ester anion (DFK precursor) to form a molecule that reverts to methyl ester upon soap removal. Initial results are encouraging but long term value is uncertain because we would be introducing a new reaction into FG-Base synthesis and this could have an impact on regulatory approval.

Removal. Attempts to remove DFK after the reaction by evaporation, adsorption, or extraction have had little effect. Identification of a selective adsorbent for DFK would be great but we have not identified any leads. Conversion of DFK to an alcohol by reaction with sodium borohydride, followed by adsorption of the alcohol onto silica gel, has been suggested by Dr. Flynn. We plan to test this idea even though long term value is uncertain because of the introduction of a new reaction into FG-Base synthesis.

Our guiding principle in pursuing DFK reduction is to understand the fundamental chemistry of both the DFK and FG reactions. In addition to testing the leads described above, Dr. Howie plans to measure the kinetics of the reaction. By knowing the activation energies, kinetic constants, and controlling concentration terms, we will be better able to identify the best reaction conditions to control DFK formation.

R G Schafermeyer

RGS/elg/2274

R. G. Schafermeyer

Keywords: difatty ketone, reaction conditions

PATENT DIVISION CORRESPONDENCE

FROM R. B. Aylor

DATE July 3, 1990

TO D. J. Bruno

RETENTION LIMIT 7/1/91

SUBJECT Examples for Process Application

ATTENTION

Attached is a draft application for the FG-Base process. It is in "near final" condition except for one or more examples of the continuous process. As soon as I receive the examples, and the next round of comments, I will try to put the case in condition for one final review before preparing the final version. I understand that there is some delay in obtaining the draft examples. If the delay continues, I will have to proceed to work on other applications that also require priority consideration. Would you please let me know when the examples will be ready?

R. B. Aylor
Patent Counsel

A17

cc: S. J. Goldstein
R. L. Hemingway
E. W. Guttag
P. J. Corrigan

PATENT DIVISION CORRESPONDENCE

FROM R. B. Aylor

DATE July 18, 1990

TO P. J. Corrigan

RETENTION LIMIT 7/1/91

SUBJECT Draft Patent Application for DR's 6644, 7102, 7788, and 7988

ATTENTION

Attached are five copies of the latest draft of the subject application for review and comments. As we discussed, we should consider whether there are additional preferred areas within the scope of the generic disclosure that should be disclosed, especially preferred combinations of improvements. Also, we agreed that you and the other technical experts will provide examples that reflect our preferred limits and examples that represent our best mode of practicing the invention.

As we also discussed, we need to decide whether to claim polyol polyesters with low levels of, e.g., difatty ketones, in this application. This decision will be based upon the potential strength and value of such claims. You have agreed to try to select limits that will distinguish the products prepared with our best processes from the products made by prior art processes. E.g., the product will be defined either as a "product by process" limited to compositions made using lower alkyl esters, or to products that contain low levels of materials that are unique to the present processes. The process of the present application produces desirably low levels of such materials. We will either redefine the processes of this application to avoid anticipating such claims, claim the compositions in this application, or claim the compositions in another application, preferably one filed at the same time as this application.

We also discussed whether we should add a disclosure of additional clean-up steps. If the steps are part of the "best mode," they will have to be disclosed in some way, even if only by exemplification. This, in turn, may complicate the filing of the present case unless these improvements are disclosed and claimed in applications that are filed promptly, preferably at the same time as this application.

In summary, the application needs to be reviewed for completeness of the disclosure and the scope of possible protection. The protection of compositions containing low levels of impurities like difatty ketones and the product purification improvements must be coordinated with this application to avoid prejudicing the coverage of those rights. The need to expand the scope of filings for maximum protection of these related areas will have to be balanced against other needs in this area and the available sources. By a copy of this communication I am soliciting input from Mr. Hemingway and Mr. Guttag on their plans for handling the coverage of polyol polyesters with low levels of impurities and/or the clean-up improvements.

R. B. Aylor

R. B. Aylor

R49
Attachments

cc: R. L. Hemingway/E. W. Guttag

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(54) Process for the synthesis of polyol fatty-acid esters.

(57) The present invention pertains to a process for the synthesis of polyol fatty-acid esters by reacting a polyol and a fatty-acid lower-alkyl ester under substantially solvent-free conditions in the presence of a transesterification catalyst and an emulsifier. The process comprises a continuous initial reaction stage in a first reaction zone wherein a steady-state conversion is achieved of over 1 % and a further reaction stage in which the reaction mixture from said first zone is further reacted to the required polyol fatty-acid esters in one or more subsequent reaction zones.

EP 0 383 404 A2

PROCESS FOR THE SYNTHESIS OF POLYOL FATTY-ACID ESTERS

The present invention relates to a process for the synthesis of polyol fatty-acid esters by reacting a polyol and a fatty-acid lower-alkyl ester under substantially solvent-free conditions in the presence of a transesterification catalyst and an emulsifier. Although applicable to the synthesis of the general group of polyol fatty-acid esters, the invention is particularly directed to the synthesis of polyol fatty-acid polyesters.

In this specification the term "polyol" is intended to include any aliphatic or aromatic compound which comprises at least four free hydroxyl groups. In particular such polyols include the group of sugar polyols, which comprise the sugars, i.e. the mono-, di- and polysaccharides, the corresponding sugar alcohols and the derivatives thereof having at least four free hydroxyl groups. Examples of sugar polyols include glucose, mannose, galactose, xylose, fructose, sorbose, tagatose, ribulose, xylulose, lactose, maltose, raffinose, cellobiose, sucrose, erythritol, mannitol, lactitol, sorbitol, xylitol and α-methylglucoside. A generally used sugar polyol is sucrose.

In this specification the term "polyol fatty-acid ester" is intended to include both the group of polyol fatty-acid oligoesters, in particular the mono-, di- and trifatty-acid esters, and the group of polyol fatty-acid polyesters, i.e. the tetra- up to the fully fatty-acid esterified polyols.

In this specification the percentage of polyol hydroxyl groups of the original polyol that on an average have been esterified with fatty acids, is referred to as the degree of polyol conversion, a degree of polyol conversion of 100 % corresponding to the fully esterified polyol.

In this specification the term "fatty acid" refers to C_8-C_{24} fatty acids which may be saturated or unsaturated, and may have straight or branched alkyl chains.

The polyol fatty-acid oligoesters are well-known for their suitability as emulsifying agents in foodstuffs and detergents, and as drying oils in paint and varnish.

The polyol fatty-acid polyesters are known to be suitable low-calorie fat-replacers in edible products. Substantially indigestible for human beings they have physical and organoleptic properties very similar to triglyceride oils and fats conventionally used in edible products. Polyol fatty-acid polyesters are further reported to have use as pharmaceutical agents in view of their ability to take up fat-soluble substances, such as in particular cholesterol, in the gastro-intestinal tract, and subsequently remove these substances from the human body.

Processes for the synthesis of polyol fatty-acid esters using transesterification reactions in substantially solvent-free systems are well known. Examples of such processes are described e.g. in US Pat. Nos 3,963,699, 4,517,360, 4,518,772 and European Pat. Nos 0 256 585, 0 254 376 and 0 301 634.

One of the main problems in prior art syntheses of polyol fatty-acid esters is caused by the heterogeneous nature of the reactant mixture at the start of the transesterification reaction. The considerable differences in polarity between the various reactants may cause partial or full de-mixing of the reactant mixture, which is very undesirable in general, but prohibitive to processes on a technical scale.

To reduce the problem of de-mixing of the reactants and to have the full amounts of reactants participate in the transesterification reaction in most cases an emulsifier is required to get a macroscopically homogeneous starting mixture. To this purpose particularly soap emulsifiers are used.

However, in conventional esterification processes on a technical scale the use of soap is frequently accompanied by viscosity problems which depending on the specific soap used may occur at introduction of the soap or the fatty acids used to produce the soap, into the reaction mixture as also at the final stages of the esterification reaction, i.e. at high degrees of conversion.

It is now an object of the present invention to provide an improved process for the synthesis of polyol fatty-acid esters, particularly with respect to avoiding initial viscosity and/or de-mixing problems, which is applicable on a technical scale.

It has now been found that the above problems which particularly occur in the very initial stage of the reaction at very low degrees of polyol conversion, can be substantially overcome by carrying out the first part of the transesterification reaction in a continuous manner. Instead of batch-wise starting each esterification process from a mix of unconverted polyol and fatty-acid lower-alkyl ester, the initial part of the reaction is carried out in a continuous manner by achieving, in a first reaction zone, a steady-state polyol conversion of over about 1% and mass-balancing under suitable reaction conditions one or more in-going reactant streams of polyol and fatty-acid lower-alkyl ester and out-going product streams of reaction mixture comprising partially converted polyol, and of lower-alkyl alcohol formed in the initial conversion. In this first zone, on an average, the polyol conversion is progressed to beyond the point where de-mixing and high viscosities occur, the steady-state reaction mixture in said first zone being capable of homogenizing and solubilizing said in-going streams of reactants.

It has further been found that by carrying out at least the initial part of the transesterification in a continuous manner, once the process has been started and is in steady-state only relatively low amounts of emulsifier are needed. The viscosity problems during the final stages of the transesterification reaction and the associated problem of refining the polyol (poly)ester product are therefore also avoided or significantly reduced.

Accordingly, the invention provides a process for the synthesis of polyol fatty-acid esters by reacting a polyol and a fatty-acid lower-alkyl ester under substantially solvent-free conditions in the presence of a transesterification catalyst and an emulsifier, said process comprising

an initial reaction stage (a) which is carried out in a first reaction zone under such conditions that the reaction mixture in said first zone is in steady-state with mass-balanced one or more in-going reactant streams into said first zone and out-going product streams from said first zone, said one or more in-going reactant streams comprising polyol and fatty-acid lower-alkyl ester, and said out-going product streams comprising reaction mixture having a polyol conversion of 1 % or more and lower-alkyl alcohol formed during the initial stage of the synthesis, and

a subsequent reaction stage (b) in which the reaction mixture from said first zone, optionally after combining with any remaining part of reactants, is further reacted to said polyol fatty-acid esters in one or more subsequent reaction zones.

This first reaction zone may be a reaction vessel fully separate from one or more further reaction vessels, but it may also be part of multi-zone continuous esterification equipment. Such multi-zone continuous esterification equipment may consist of a serial sequence of separate reaction vessels as also of e.g. a multi-tray column reactor with cross-flow or counter-current stripping equipment, or a combination thereof.

The reactants which are fed to the first reaction zone on a continuous basis and in mass balance with the out-going product streams from this first zone, are a polyol and a fatty-acid lower-alkyl ester. The polyol and the fatty-acid lower-alkyl ester may be introduced into the first reaction zone as separate streams, but are generally and preferably combined in a single in-going stream.

Under steady-state conditions the one or more in-going reactant streams of polyol and fatty-acid lower-alkyl ester should be in mass balance with the out-going product streams of the reaction mixture comprising the partially converted polyol, and of lower-alkyl alcohol formed during the initial reaction stage. In the first reaction zone steady-state polyol conversions should be achieved of over 1 %, and in general suitable conversions lie within the range of from 2 to 60 %, in particular, 3 to 50 %. Polyol conversions of over 60 % in the first reaction zone in general carry a prohibitive cost penalty. Preferred steady-state polyol conversions lie within the range of from 10 to 40 % and conversions of within the range of 15 to 30 or even to 25 % have been found to give best results.

The polyol can be any of those as defined hereinbefore, or a mixture thereof. Preferred polyol starting materials are the sugar polyols, and in particular sucrose.

Suitable fatty-acid lower-alkylesters are fatty-acid esters of the group of lower alcohols including mono-, di- and triols. In particular, the ester is derived from the C_1-C_5 mono-alcohols, preferably methanol. The fatty-acid residues can be any of those as defined hereinbefore, the selection of which is dependent of the specific polyol fatty-acid esters desired.

The amount of fatty-acid lower-alkylester is dependent on the desired degree of conversion. In general excess amounts of fatty-acid lower-alkylester are used. More particularly, when fully converted sucrose polyesters are aimed at, good results are obtained when a molar ratio of fatty-acid lower-alkylester : sucrose is used within the range of from 10:1 to 20:1, and preferably of from 10.5:1 to 18:1, or even from 10.5:1 to 14:1.

It is not necessary to introduce the full amount of all the reactants, in particular the fatty-acid lower-alkyl ester, into the first reaction zone, but part may also be added to the reaction mixture at a later stage of the transesterification reaction. Particularly, in the synthesis of polyol fatty-acid polyesters having very specific fatty-acid compositions, e.g. a combination of two or more sharp fatty-acid fractions, addition of different fractions of fatty-acid lower-alkyl esters corresponding to such sharp fatty-acid fractions during later stages of the esterification reaction may be desirable or necessary.

Suitable transesterification catalysts include the group consisting of alkali metals, alkaline earth metals, and alloys thereof, as well as the alkoxides, bicarbonates, carbonates, hydrides, and hydroxides of such metals. KOH has been found to be particularly suitable, but also NaOH and the corresponding carbonates, and bicarbonates of potassium or sodium can be advantageously used. Although one might argue that the above reagents are not the catalysts themselves, but are reagents forming the catalyst, in this specification as is done in the literature relating to similar processes, this group will be referred to as catalysts.

In general the catalyst is introduced into the first reaction zone as part of the in-going stream containing

the polyol. Part of the polyol will have reacted with the catalyst under formation of the polyol anion which in the reaction is believed to be the actual catalyzing agent.

The catalyst is used in an amount corresponding to a molar ratio of catalyst : polyol of at least 0.01:1, and in particular of within the range of 0.05:1 to 1:1. Preferred catalyst : polyol ratios lie within the range of 0.1:1 to 0.3:1, best results having been found with ratios within the range of from 0.2:1 to 0.3:1.

During the start-up of the process in accordance with the present invention an emulsifier should be introduced to improve contact between the various reactants particularly in said first reaction zone. Many types of alkali-resistant emulsifiers can suitably be used, such as edible emulsifiers including phosphatides, such as lecithin, mono- and diglycerides and sugar oligoesters of fatty acids, in particular the mono-and diesters, and detergents, such as soaps and alkali metal alkyl sulphates.

Preferred emulsifiers are alkali metal soaps derived from any of the fatty acids as defined hereinbefore. It has been found that conversion rates of polyol to polyol fatty-acid ester are improved as also any viscosity problems during the final stages of the esterification reaction are avoided when fatty-acid soap emulsifiers are used comprising at least 15% by weight short-chain fatty acid soaps. Preferred levels of short chain fatty-acid soap are 75 to 100% by weight. Such short chain fatty-acid soaps are characterized by a fatty-acid chain lengths of less than 15 carbon atoms, and in particular within the range of 6 to 14 carbon atoms, such as coconut soap.

Suitable amounts of emulsifier in the first reaction zone in general lie within the range of from 0.1 to 15% by weight of the total reactant mixture, and in particular, of from 0.2 to 12%, amounts of 1 to 4% by weight being preferred. At the start-up of the reaction such amounts of emulsifier are introduced into the first reaction zone preferably as part of the one or more in-going reactant streams of polyol and lower-alkyl fatty-acid ester, during steady-state conditions in the first reaction zone the emulsifier may also be introduced by recirculation from further stages of the esterification reaction. The molar ratio of emulsifier to polyol during steady-state conditions in the first reaction zone preferably is within the range of 0.2:1 to 0.8:1, molar ratios of 0.3:1 to 0.7:1, such as about 0.4:1 being preferred most.

Particularly, when the emulsifier is selected from the group of alkali metal soaps, it may be convenient, before introduction into the first reaction zone, to first dissolve the corresponding fatty acids in the lower-alkyl fatty acid ester and neutralize with an alkaline material, such as KOH.

Optionally, before introduction of the various components into the first reaction zone one or more solvents may be used to improve addition and mixing thereof. Suitable solvents include water and/or lower alcohols, such as C_1-C_5 alcohols, in particular methanol.

It is an essential feature of the processes in accordance with the present invention that before introduction into the first reaction zone any such solvents are substantially removed to achieve in the first reaction zone substantially solvent-free reaction conditions.

By substantially solvent-free reaction conditions is meant less than 0.5 % by weight of solvent, in particular of water. In principle solvent levels at the start-up of the transesterification reaction should be as low as possible, but to some extent will be determined by economic considerations. Solvent levels of less than 0.1 % by weight and particularly of from 0.01 % to 0.08 % by weight are preferred, effecting levels of below 0.01 % by weight getting prohibitively expensive.

De-solvatizing of the various components or component mixes may be suitably achieved by way of spray-drying which may be carried out at introduction into the first reaction zone, but preferably before such introduction, by passing the mixture through a spraying nozzle under drying conditions.

It may be of further advantage to pre-homogenize streams of combined components fed to the first reaction zone before the passing thereof through the spraying nozzle by an alternative agitation step for example employing a dynamic or static mixer, or flow restriction in the feed line to the spraying nozzle.

Preferably, in the first reaction zone agitation is applied to ensure thorough mixing of the reaction components and to aid the removal of the lower- alkyl alcohols which are formed during the transesterification reaction. Such agitation is suitably achieved by stirring.

The streams of reactants to and from the first reaction zone should be such that under the temperature and pressure conditions described hereunder in more detail, the average residence time of the reaction mixture in the first zone is caused to be within the range of 1 to 4 hours, in particular of 1.2 to 3 hours. To minimize the risk of non-participating polyol average residence times in the range of from 1.5 to 2.5 are preferred, best results being obtained using residence times in the range of from 1.7, and particularly 1.8, to 2.2 hours.

In accordance with the process of the present invention the out-going reaction mixture from the first reaction zone is subsequently further reacted under suitable conditions to cause transesterification to the desired polyol fatty-acid esters. This may be carried out both batch-wise or continuously.

In general, the transesterification reaction both in the first reaction zone and in the subsequent further

reaction is carried out at elevated temperature, in particular, in the range of from 100 to 180 °C, a reaction temperature in the range of 110 to 160 °C being preferred, temperatures in the range of from 120 to 150 °C or even 130 to 140 °C being preferred most.

The reaction is carried out under such conditions that the lower-alkyl alcohols formed in the transesterification, are removed during the reaction. To this purpose the reaction is advantageously carried out at reduced pressure in terms of the partial vapour pressure of the lower-alkyl alcohol. Suitably such partial vapour pressures in the first reaction zone are reduced to levels within the range of from 20 to 200 mbar, pressures of 35 to 150 and particularly of 40 to 125 mbar being preferred. Best results are obtained with prssure levels of from 40 to 100 mbar. During the reaction subsequent to the first reaction zone pressures are applied as low as possible, such as below 50 mbar and in particular below 25 mbar. When full esterification of the polyol is aimed at, the partial vapour pressure of the lower-alkyl alcohol is preferably reduced to a level of less than 10 mbar, and most preferably to a level of less than 5 mbar. These pressures may be achieved by gradual pressure reduction over time in a batch-wise process, but also by a step-wise pressure reduction over two or more reaction compartments or zones in a continuous process.

Particularly during the final stage of a batch-wise process or in the final reaction zone of a continuous process, a preferred method to reduce the lower-alkyl alcohol partial vapour pressure is to use a stripping agent to ensure adequate removal of the lower-alkyl alcohol formed during the transesterification reaction. Suitable such stripping agents include inert gases, such as nitrogen, and volatile (under reaction conditions) organic compounds having low or no oxidating tendency. A particularly preferred stripping agent of the latter type is hexane.

Appropriate amounts of stripping agent through the reaction mixture are dependent upon the reaction conditions and the set-up and dimensions of the equipment. In general, suitable amounts of stripping agent during the final stages of the reaction lie within the range of 1000 to 4000 litres of stripping agent per kg of reaction mixture, amounts within the range of 2000 to 3000 litres/kg being preferred.

Although often suitable partial vapour pressures during earlier stages of the transesterification reaction can be achieved without the use of stripping agents, if it is desired to use stripping agents also during these stages of the transesterification reaction, only lower amounts of stripping agent are needed. Being somewhat dependent upon the molar ration of polyol versus fatty-acid lower-alkyl ester, suitable amounts of stripping agent during the initial stages preferably are selected within the range of 30 to 700 litres/kg, and in particular within the range of 60 to 300 litres/kg.

The amount of stripping agent is expressed as litres per kg of reaction mixture under the pressure and temperature conditions of the reaction mixture at the moment of stripping.

Suitable contact between the stripping agent and the reaction mixture is normally established due to the whirling action caused by the stripping agent flowing through the reaction mixture. However, it may be desirable to apply further agitation by way of appropriate stirrer means.

Preferably, after leaving the reaction mixture the stripping agent is first, at least partly, separated from the lower alkyl alcohol, and subsequently recirculated to the reaction mixture.

Although the process of the present invention is suitable for the synthesis of both polyol fatty-acid oligoesters and polyesters as defined hereinbefore, it is particularly directed to the synthesis of the polyester group. The polyesters will in general be characterised by a degree of polyol conversion of 70 % or more, degrees of polyol conversion of 80 % or more, or even of 90 % or more being preferred. In particular, such polyesters derived from the sugar polyols selected from the group of disaccharides or the alcohol derivatives thereof, such as sucrose, and esterified to a degree of polyol conversion of 95 % or more, or even of 98 % or more, are suitably and preferably synthesized by the method in accordance with the present invention.

The invention will now be illustrated more specifically in the following experimental examples.

Where a full synthesis was tested the processes described in the following examples were carried out in a reactor configuration consisting of a pre-reactor and a main reactor.

The pre-reactor (which corresponds to the first reaction zone in accordance with the invention) consisted of a cylindrical reaction vessel provided with means for stirring and heating, in- and outlets for stripping agent, a peristaltic-pump driven feed for the in-going stream of reactants and a peristaltic-pump driven suction line for the out-going product stream of reaction mixture from the pre-reactor to the main reactor. The inlet point of the suction line in the pre-reactor was such that all fluids above a certain point were removed.

As the main reactor a three-tray column reactor with means for heating and counter-current stripping was used.

In the examples 1 to 11 the polyol was sucrose, the transesterification catalyst was potassium hydroxide, the emulsifier was the potassium soap of coconut fatty acids and the fatty-acid lower-alkyl ester

was the methanol ester of fatty acids derived from partially hardened soybean oil (hardened to a melting point of 28 °C). These reactants were introduced in the pre-reactor in the form of a single stream formed by combining a concentrated slurry (about 10-15 %) of the coconut soap in part of the soybean methanol ester with a sucrose/KOH dispersion (about 10 %) in the remainder of the soybean methanol ester.

In both the pre-reactor and the main reactor partial methanol pressures were reduced by way of stripping. As stripping agent nitrogen gas was used.

In the examples all percentages are expressed by weight of the total reaction mixture unless indicated otherwise.

EXAMPLE 1

The reactant feed to the pre-reactor consisted of:

sucrose	6.24%
KOH	0.27%
soap (*)	3.13%
soybean methanol ester	90.30%
water	0.06%

(*) 2.8% of coconut soap plus 0.3% of soybean soap due to partial conversion of the soybean methanol ester.

In terms of molar ratios these amounts corresponded to:

KOH : sucrose	0.27 : 1
soap : sucrose	0.65 : 1
soybean methanol ester : sucrose	16.7 : 1

The reaction conditions in the pre-reactor (volume about 1 litre) were:

temperature	135 °C
partial methanol pressure	55 mbar
stirring power input per volume of reaction mixture	4-5 W/l
stripping gas volume per weight of reactant feed	149 l/kg (*)
average residence time of reaction mixture in pre-reactor	1.8 hours

(*) under reaction conditions

Reaching steady-state in about 2.5 average residence times after start-up, the composition of the out-going product stream of reaction mixture from the pre-reactor which was fed to the first compartment of the main reactor, was:

sucrose oligoester (degree of conversion: 16.7%)	12.71%
sucrose	0.02%
KOH	0.11%
soap	3.90%
soybean methanol ester	82.97%

The reaction conditions in the various compartments of the main reactor (total reactor volume of about 3

litres) were:

	reactor compartments		
	1	2	3
temperature (°C)	137°C	133°C	137°C
average residence time (hours)	1.7 h	1.9 h	2.0 h
partial methanol pressure (*)	16 mbar	5 mbar	1 mbar
degree of conversion of sucrose polyester	71.1%	91.1%	96.6%
(*) stripping gas volume per weight of reactant feed	2500 l/kg		

The composition of the final product from the main reactor was:

sucrose polyester (degree of conversion: 96.6%)	45.60%
sucrose	0.00%
KOH	0.04%
soap	4.16%
soybean methanol ester	49.59%
water	0.02%

EXAMPLE 2

The reactant feed to the pre-reactor consisted of:

sucrose	6.23%
KOH	0.25%
coconut soap (*)	3.15%
soybean methanol ester	90.33%
water	0.04%

(*) includes 0.30% of soybean methanol ester derived soap

In terms of molar ratios these amounts corresponded to:

KOH : sucrose	0.25 : 1
soap : sucrose	0.65 : 1
soybean methanol ester : sucrose	16.8 : 1

The reaction conditions in the pre-reactor (0.79 kg reaction mixture) were:

temperature	135 °C
partial methanol pressure	46 mbar
stirring power input per volume of reaction mixture	4-5 W/l
stripping gas volume per weight of reactant feed	268 l/kg (*)
average residence time of reaction mixture in pre-reactor	1.9 hours

(*) under reaction conditions

Reaching steady-state in about 2.5 average residence times after start-up, the composition of the out-going product stream of reaction mixture from the pre-reactor was:

sucrose oligoester (degree of conversion: 25.6%)	16.27%
sucrose	0.00%
KOH	0.06%
soap	4.11%
soybean methanol ester	79.22%

EXAMPLE 3

The reactant feed to the pre-reactor consisted of:

sucrose	6.10%
KOH	0.27%
coconut soap (*)	2.84%
soybean methanol ester	90.69%
water	0.10%

(*) includes 0.30% of soybean methanol ester derived soap

In terms of molar ratios these amounts corresponded to:

KOH : sucrose	0.27 : 1
soap : sucrose	0.60 : 1
soybean methanol ester : sucrose	17.2 : 1

The reaction conditions in the pre-reactor (0.77 kg reaction mixture) were:

temperature	135 °C
partial methanol pressure	42 mbar
stirring power input per volume of reaction mixture	4-5 W/l
stripping gas volume per weight of reactant feed	364 l/kg (*)
average residence time of reaction mixture in pre-reactor	2.0 hours

(*) under reaction conditions

Reaching steady-state in about 2.5 average residence times after start-up, the composition of the out-going product stream of reaction mixture from the pre-reactor was:

sucrose oligoester (degree of conversion: 32.2%)	18.50%
sucrose	0.00%
KOH	0.04%
soap	3.82%
soybean methanol ester	77.01%

EXAMPLE 4

The reactant feed to the pre-reactor consisted of:

sucrose	6.72%
KOH	0.48%
coconut soap (*)	3.21%
soybean methanol ester	89.52%
water	0.07%

(*) includes 0.3% of soybean methanol ester derived soap

In terms of molar ratios these amounts corresponded to:

KOH : sucrose	0.44 : 1
soap : sucrose	0.62 : 1
soybean methanol ester : sucrose	15.4 : 1

The reaction conditions in the pre-reactor (0.73 kg reaction mixture) were:

temperature	136 °C
partial methanol pressure	42 mbar
stirring power input per volume of reaction mixture	4-5 W/l
stripping gas volume per weight of reactant feed	142 l/kg (*)
average residence time of reaction mixture in pre-reactor	1.8 hours

(*) under reaction conditions

Reaching steady-state in about 2.5 average residence times after start-up, the composition of the out-going product stream of reaction mixture from the pre-reactor was:

sucrose oligoester (degree of conversion: 10.3%)	10.73%
sucrose	0.19%
KOH	0.13%
soap	4.67%
soybean methanol ester	82.82%

EXAMPLE 5

The reactant feed to the pre-reactor consisted of:

sucrose	6.80%
KOH	0.31%
coconut soap (*)	3.25%
soybean methanol ester	89.57%
water	0.07%

(*) includes 0.3% of soybean methanol ester derived soap

In terms of molar ratios these amounts corresponded to:

KOH : sucrose	0.28 : 1
soap : sucrose	0.62 : 1
soybean methanol ester : sucrose	15.2 : 1

The reaction conditions in the pre-reactor (0.77 kg reaction mixture) were:

temperature	135 °C
partial methanol pressure	41 mbar
stirring power input per volume of reaction mixture	4-5 W/l
stripping gas volume per weight of reactant feed	518 l/kg (*)
average residence time of reaction mixture in pre-reactor	1.8 hours

(*) under reaction conditions

Reaching steady-state in about 2.5 average residence times after start-up, the composition of the out-going product stream of reaction mixture from the pre-reactor was:

sucrose oligoester (degree of conversion: 41.5%)	23.71%
sucrose	0.28%
KOH	0.11%
soap	4.11%
soybean methanol ester	71.22%

EXAMPLE 6

The reactant feed to the pre-reactor consisted of:

sucrose	5.99%
KOH	0.26%
coconut soap (*)	2.07%
soybean methanol ester	91.63%
water	0.05%

(*) includes 0.3% of soybean methanol ester derived soap

In terms of molar ratios these amounts corresponded to:

KOH : sucrose	0.26 : 1
soap : sucrose	0.45 : 1
soybean methanol ester : sucrose	17.7 : 1

The reaction conditions in the pre-reactor (0.77 kg reaction mixture) were:

temperature	135 °C
partial methanol pressure	86 mbar
stirring power input per volume of reaction mixture	4-5 W/l
stripping gas volume per weight of reactant feed	95 l/kg (*)
average residence time of reaction mixture in pre-reactor	1.9 hours

(*) under reaction conditions

Reaching steady-state in about 2.5 average residence times after start-up, the composition of the out-going product stream of reaction mixture from the pre-reactor was:

sucrose oligoester (degree of conversion: 20.2%)	12.33%
sucrose	0.55%
KOH	0.12%
soap	2.73%
soybean methanol ester	83.97%

EXAMPLE 7

The reactant feed to the pre-reactor consisted of:

sucrose	5.89%
KOH	0.39%
coconut soap (*)	3.47%
soybean methanol ester	90.17%
water	0.08%

(*) includes 0.3% of soybean methanol ester derived soap

In terms of molar ratios these amounts corresponded to:

KOH : sucrose	0.40 : 1
soap : sucrose	0.76 : 1
soybean methanol ester : sucrose	17.7 : 1

The reaction conditions in the pre-reactor (88 kg reaction mixture) were:

temperature	135° C
partial methanol pressure	50 mbar
stirring power input per volume of reaction mixture	4-5 W/l
stripping gas volume per weight of reactant feed	166 l/kg (*)
average residence time of reaction mixture in pre-reactor	1.9 hours

(*) under reaction conditions

Reaching steady-state in about 2.5 average residence times after start-up, the composition of the out-going product stream of reaction mixture from the pre-reactor which was fed to the main reactor (identical to the pre-reactor), was:

sucrose oligoester (degree of conversion: 18.5%)	12.44%
sucrose	0.13%
KOH	0.12%
soap	3.17%
soybean methanol ester	83.46%

The reaction conditions in the main reactor (104 kg reaction mixture) were:

temperature (° C)	136° C
average residence time (hours)	2.2 h
partial methanol pressure (*)	39 mbar
(*) stripping gas volume per weight of reactant feed	261 l/kg

The composition of the final product from the main reactor was:

sucrose polyester (degree of conversion: 40.7%)	20.81%
sucrose	0.00%
KOH	0.07%
soap	5.10%
soybean methanol ester	74.00%
water	0.02%

EXAMPLE 8

The reactant feed to the pre-reactor consisted of:

sucrose	14.05%
KOH	0.57%
coconut soap (*)	5.38%
soybean methanol ester	79.86%
water	0.14%

(*) includes 0.55% of soybean methanol ester derived soap

In terms of molar ratios these amounts corresponded to:

KOH : sucrose	0.25 : 1
soap : sucrose	0.49 : 1
soybean methanol ester : sucrose	6.57 : 1

The reaction conditions in the pre-reactor (0.64 kg reaction mixture) were:

temperature	135 °C
partial methanol pressure	42 mbar
stirring power input per volume of reaction mixture	4-5 W/l
stripping gas volume per weight of reactant feed	602 l/kg (*)
average residence time of reaction mixture in pre-reactor	1.7 hours

(*) under reaction conditions

Reaching steady-state in about 2.5 average residence times after start-up, the composition of the out-going product stream of reaction mixture from the pre-reactor was:

sucrose oligoester (degree of conversion: 22.8%)	33.89%
sucrose	1.22%
KOH	0.24%
soap	6.87%
soybean methanol ester	57.78%

EXAMPLE 9

The reactant feed to the pre-reactor consisted of:

sucrose	9.24%
KOH	0.36%
coconut soap (*)	4.32%
soybean methanol ester	85.96%
water	0.12%

(*) includes 0.45% of soybean methanol ester derived soap

In terms of molar ratios these amounts corresponded to:

KOH : sucrose	0.24 : 1
soap : sucrose	0.60 : 1
soybean methanol ester : sucrose	10.7 : 1

The reaction conditions in the pre-reactor (0.75 kg reaction mixture) were:

temperature	136 °C
partial methanol pressure	42 mbar
stirring power input per volume of reaction mixture	4-5 W/l
stripping gas volume per weight of reactant feed	373 l/kg (*)
average residence time of reaction mixture in pre-reactor	1.9 hours

(*) under reaction conditions

Reaching steady-state in about 2.5 average residence times after start-up, the composition of the out-going product stream of reaction mixture from the pre-reactor was:

sucrose oligoester (degree of conversion: 22.2%)	21.91%
sucrose	0.48%
KOH	0.09%
soap	5.71%
soybean methanol ester	71.76%

EXAMPLE 10

The reactant feed to the pre-reactor consisted of:

sucrose	5.51%
KOH	0.27%
coconut soap (*)	2.01%
soybean methanol ester	92.17%
water	0.04%

(*) includes 0.55% of soybean methanol ester derived soap

In terms of molar ratios these amounts corresponded to:

KOH : sucrose	0.30 : 1
soap : sucrose	0.47 : 1
soybean methanol ester : sucrose	21.6 : 1

The reaction conditions in the pre-reactor (0.90 kg reaction mixture) were:

temperature	136 °C
partial methanol pressure	45 mbar
stirring power input per volume of reaction mixture	4-5 W/l
stripping gas volume per weight of reactant feed	155 l/kg (*)
average residence time of reaction mixture in pre-reactor	2.5 hours

(*) under reaction conditions

Reaching steady-state in about 2.5 average residence times after start-up, the composition of the out-going product stream of reaction mixture from the pre-reactor which was fed to the main reactor (identical to the

pre-reactor), was:

sucrose oligoester (degree of conversion: 18.5%)	10.23%
sucrose	0.83%
KOH	0.09%
soap	2.70%
soybean methanol ester	86.22%

The reaction conditions in the main reactor (0.51 kg reaction mixture) were:

temperature (°C)	135°C
average residence time (hours)	1.4 h
partial methanol pressure (*)	16 mbar
(*) stripping gas volume per weight of reactant feed	1315 l/kg

The composition of the final product from the main reactor was:

sucrose polyester (degree of conversion: 67.0%)	27.36%
sucrose	0.26%
KOH	0.07%
soap	3.53%
soybean methanol ester	68.79%

EXAMPLE 11

The reactant feed to the pre-reactor consisted of:

sucrose	7.50%
KOH	0.31%
coconut soap (*)	2.80%
soybean methanol ester	89.33%
water	0.06%

(*) includes 0.3% of soybean methanol ester derived soap

In terms of molar ratios these amounts corresponded to:

KOH : sucrose	0.25 : 1
soap : sucrose	0.48 : 1
soybean methanol ester : sucrose	13.8 : 1

The reaction conditions in the pre-reactor (0.74 kg reaction mixture) were:

temperature	135 °C
partial methanol pressure	51 mbar
stirring power input per volume of reaction mixture	4-5 W/l
stripping gas volume per weight of reactant feed	310 l/kg (*)
average residence time of reaction mixture in pre-reactor	1.9 hours

(*) under reaction conditions

Reaching steady-state in about 2.5 average residence times after start-up, the composition of the out-going product stream of reaction mixture from the pre-reactor was:

sucrose oligoester (degree of conversion: 27.1%)	19.97%
sucrose	1.14%
KOH	0.12%
soap	3.81%
soybean methanol ester	74.96%

Claims

1. A process for the synthesis of polyol fatty-acid esters by reacting a polyol and a fatty-acid lower-alkyl ester under substantially solvent-free conditions in the presence of a transesterification catalyst and an emulsifier, characterized in that the process comprises
an initial reaction stage (a) which is carried out in a first reaction zone under such conditions that the reaction mixture in said first zone is in steady-state with mass-balanced one or more in-going reactant streams into said first zone and out-going product streams from said first zone, said one or more in-going reactant streams comprising polyol and fatty-acid lower-alkyl ester, and said out-going product streams comprising reaction mixture having a polyol conversion of 1 % or more and lower-alkyl alcohol formed during the initial stage of the synthesis, and
a subsequent reaction stage (b) in which the reaction mixture from said first zone, optionally after combining with any remaining part of reactants, is further reacted to said polyol fatty-acid esters in one or more subsequent reaction zones.

2. A process according to claim 1 wherein the emulsifier is an alkali metal soap.

3. A process according to claim 2 wherein the alkali metal soap is selected from the group of short chain soaps having a chain length within the range of from 6 to 14 carbon atoms.

4. A process according to any one of the preceding claims wherein the fatty-acid lower-alkyl ester is a fatty-acid methyl ester.

5. A process according to any one of the preceding claims wherein the transesterification catalyst is selected from the group consisting of hydroxides, carbonates and bicarbonates of potassium and sodium.

6. A process according to any one of the preceding claims wherein the reaction mixture in said first reaction zone has a degree of polyol conversion of within the range of from 10 to 40 %.

7. A process according to any one of the preceding claims wherein the reaction mixture in said first zone has a solvent level of 0.1 % by weight or less.

8. A process according to any one of the preceding claims wherein the reaction temperature in said first zone is maintained at a level of within the range of from 120 to 150 °C.

9. A process according to any one of the preceding claims wherein the partial vapour pressure of the fatty-acid lower-alkyl ester in said first reaction zone is reduced to a level of within the range of from 40 to 125 mbar.

10. A process according to claim 9 wherein the partial vapour pressure is reduced by the use of a stripping agent.

11. A process according to claim 10 wherein the stripping agent is used in an amount within the range of from 60 to 300 litres stripping agent per kg of reaction mixture.

12. A process according to any one of the preceding claims wherein the average residence time of the

reaction mixture in said first zone is caused to be within the range of from 1.5 to 2.5 hours.

13. A process according to any one of the preceding claims wherein the molar ratio of transesterification catalyst to polyol in said first reaction zone is within the range of from 0.1:1 to 0.3:1.

14. A process according to any one of the preceding claims wherein the molar ratio of emulsifier to polyol in said first reaction zone is within the range of from 0.2:1 to 0.8:1.

15. A process according to any one of the preceding claims for the synthesis of polyol fatty-acid polyesters.

16. A process according to claim 15 for the synthesis of polyol fatty-acid polyesters having a polyol conversion of 90 % or more.

17. A process according to any one of the preceding claims wherein the polyol is sucrose.

18. A process according to claim 15 wherein the molar ratio of fatty-acid lower-alkyl ester to sucrose is within the range of from 10:5:1 to 18:1.

19. A process according to any one of the preceding claims wherein said first reaction zone is fully separate from said one or more subsequent reaction zones.

20. A process according to any one of the preceding claims wherein said one or more subsequent reaction zones are compartments of a multi-tray column reactor.